Paint and Coating Testing Manual

Joseph V. Koleske
editor

ASTM

Fourteenth Edition of the Gardner-Sward Handbook

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Joseph V. Koleske, Editor

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Foreword

THIS PUBLICATION, *Paint and Coating Testing Manual: Fourteenth Edition of the Gardner-Sward Handbook*, was sponsored by Committee D-1 on Paint and Related Coatings, Materials, and Applications. The editor was Joseph V. Koleske. This is Manual 17 in ASTM's manual series.

Acknowledgments

ASTM WOULD LIKE TO EXPRESS its gratitude to the authors of the previous 13 editions of this publication. These publications made significant contributions to the technology; therefore, ASTM, in its goal to publish books of technical significance, called upon current experts in the field to revise and update this important publication to reflect the changes and advancements that have taken place since the last edition, which was published in 1972.

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Preface

AT A JANUARY 1967 MEETING OF ASTM COMMITTEE D-1 held in Washington, DC, ASTM (American Society for Testing and Materials) accepted ownership of the *Gardner-Sward Handbook* from the Gardner Laboratory. It was through this laboratory that Dr. Henry A. Gardner published the previous twelve editions of the manual. Acceptance of this ownership gave ASTM an assumed responsibility for revising, editing, and publishing future editions of this well-known, respected manual. The undertaking was assigned to Committee D-1 on Paint and Related Coatings, Materials, and Applications. This committee established a permanent subcommittee, D01.19 on Gardner-Sward Handbook, chaired by John C. Weaver, to provide technical, editorial, and general policy guidance for preparation of the 13th and subsequent editions of the *Gardner-Sward Handbook*. The 13th edition was published in 1972 as the *Paint Testing Manual* (STP 500) with Mr. G. G. Sward as editor. The manual has served the industry well for the past two decades; it contains useful information that cannot be found elsewhere. However, the passage of more than 20 years since its publication is readily apparent in many and perhaps most chapters of the manual.

Although updating the manual was discussed through the years, a variety of reasons prevented this task from being accomplished. Feasibility of updating the manual was not realized until mid-1989 when Dr. John J. Brezinski, Union Carbide (retired), and Mrs. Kathleen A. Dernoga, Manager of Acquisitions and Review of ASTM Technical Books and Journals, discussed the matter and the 14th edition was conceived. Between then and the spring of 1990 an outline for the 14th edition was developed and was approved by members of Subcommittee D01.19. Almost five years later the manual was completed—no wonder such a long period elapsed between editions!

The scope of the new edition is in keeping with the stated scope of Subcommittee D01.19:

> "To provide technical, editorial, and general policy guidance for preparation of the Fourteenth and subsequent editions of the Gardner-Sward Handbook. The handbook is intended for review of both new and experienced paint technologists and the past, present, and foreseeable trends in all kinds of testing within the scope of Committee D-1. It supplements, but does not replace, the pertinent parts of the Society's Book of Standards. It describes briefly and critically all Test Methods believed to have significance in the world of paint technology, whether or not these tests have been adopted officially by the society."

In this new edition, ASTM standard methods are described by minimal detail with the various volumes of the *ASTM Book of Standards* remaining the primary source of such information. An effort was made to include references in the absence of ASTM information concerning industrial, other society, national, and international test methods. For the most part, the manual contains either new chapters or the old topics/chapters in rewritten form. In a few cases, the old manual was merely updated, attesting to either the quality of the earlier writing, the lack of development in the area, or the apparent waning of interest in the topic. A variety of modern topics has been included. Individual authors, experts in their various fields, were given a great deal of freedom in expressing information about their topics.

Many things have changed through the years. The chemical emphasis has shifted from natural products to synthetic products, so this edition of the manual contains chapters that deal with a large number of synthetic polymers used in the coating industry. Instrumentation has undergone a marked change with innovative electronics providing the key to many changes. An effort was made to include chapters dealing with a broad variety of instruments.

To the authors, a warm, heart-felt "thank you." You put your talents to work and sacrificed much personal time to make the manual a success. A "thank you" is also due the reviewers, who are a special lot. They must be critical, yet carry out their task in a constructive manner. Because of the customary anonymity accorded reviewers, they should know that some authors made a special effort to express their appreciation for the review comments that they felt strengthened their manuscripts. Those organizations who permitted authors' time, use of support staff, and supplies are truly appreciated. Works such as this manual could not be completed without their generosity—may they prosper. The staff at ASTM is distinctive—they were interested and smilingly helpful to the authors, reviewers, Subcommittee D01.19, and the editor as they guided us through the maze of the publication assembly process (though they may have gritted their teeth at times). A very special thanks to Monica Siperko of ASTM, who worked closely with the editor in dealing with authors, reviewers, ASTM staff, and manuscripts. Her invaluable, cheerful assistance is appreciated. And last, but certainly not least, the contributions of Maureen Quinn and David Jones of the ASTM editing staff are acknowledged. Their able assistance ensured that the manual was uniform in style and grammar.

Joseph V. Koleske
Editor

Introduction

PAST TO PRESENT

More than a score of years has passed since the previous edition of this manual was published, and many changes have taken place in the coating industry and elsewhere since that time. In 1972, the previous publication date, over 90% of all industrial coatings were low-solids, solvent-borne coatings. Total solids ranged from about 5 to 20% by weight. In the early 1970s, solvents were inexpensive, convenient carriers for the binder polymers used in coatings, and there appeared to be little knowledge in the scientific community about the consequences of breathing them, absorbing them through the skin, or placing them either in the atmosphere or in the environment in general. There were exceptions, as when a particular compound was known to be highly toxic. The specific effect of certain solvents as well as other chemicals on certain segments of the population was unknown in the scientific community. Large quantities of solvent were needed to dilute the high-molecular-weight binders to an appropriate application viscosity. High-molecular-weight binders imparted high-quality characteristics to the final coating. In addition, very dilute solutions allowed application of very thin, but continuous, films. These factors coupled with the low cost of energy used to drive the large ovens associated with coating manufacture were major reasons that kept coating systems low in solids and solvent-borne in nature. Even a large percentage of architectual coatings was oil-based, solvent-borne formulations. In an overall sense, products of the coatings industry worked and did a satisfactory job.

However, new technologies were being talked about, worked on, and even commercialized, albeit in a small way. Terms such as "powder coatings," "radiation-cure coatings," and "water-borne coatings" were beginning to creep into the language of the coating industry. The technologies promised a great deal, were considered mainly by the innovative, and had many difficulties associated with their introduction. Abbreviations such as EPA, MSDS, OSHA, SARA, TSCA, and similar others that are familiar to us today weren't yet in the industry's jargon. In fact, less than two pages (pp. 418–419) in the previous edition of this manual were dedicated to the topic of atmospheric pollution, and therein basically only Rule 66 was briefly discussed. No criticism is meant—such was the nature of the topic in the pre-1972 world. As stated previously, "Times have changed," and this new edition devotes a significantly sized chapter to acquaint readers briefly with the topic of regulation of volatile organic compounds emitted from coatings. This topic and the related topics of health and safety are mentioned a number of times in the manual.

POWDER COATINGS

Changes other than those of regulation, though related, have taken place in our industry. In 1972, coating journals had discussions about the "powder explosion." Powder coatings were to take over the industry since they were clean, 100% solids systems that could be applied on any substrate that could be either heated for fluid-bed application or made conductive for electrostatic spray application. Although powder coatings had been used in Europe as early as the 1950s, not many powder-coating systems existed in the United States in the 1970s. There was little incentive for large-company, raw-material suppliers who sold solvents to get into the powder coating business. A prime obstacle was the fact that there was little one could do to alter a

powder coating once it was made. If a fully formulated product such as a powder coating were to be sold by a raw-material supplier, there was a feeling that customers for solvents and other raw materials would be alienated. Also, from the end-user point of view, conversion from in-place, existing application equipment to powder coating equipment required a capital expenditure. This is a factor that always was and still can be a hindrance to conversion from existing to new technology.

It did not take long for the fuse of the powder keg to fizzle—but, more importantly, it did not go out. Epoxide powders were in vogue for pipeline coatings and were used on the Alaskan pipeline. In the early days of powder coatings, small amounts of vinyl chloride homopolymer and copolymer, polyester, and nylon powders were used. Fluid-bed application methods were first to be commercialized. It was relatively easy to melt-mix and grind mixtures of polymers, pigments, plasticizers, and other formulating ingredients to obtain the relatively large particle-size powders used by this method. Electrostatic spray took longer to develop since procedures for manufacture of the fine particle-size powders as well as the sophisticated spray equipment needed for effectively and efficiently handling charged powder particles had to be developed.

Powder coatings not only had problems in manufacture and application, but also in other areas such as: changeover from one color, availability and storage of a number of colored powders, flow and leveling, in developing thermoset coatings that would flow and level before cross-linking at an elevated temperature, in blocking during storage and as the powder flowed through the spray-system hoses and gun, in cost coupled with concerns about handling overspray and recovery and disposal. But, something new had been born, and a new industry within the coating industry was going through the throes of growing up in a competitive environment. Today the powder industry segment is strong and is growing. It has developed to the point where it now has its own organization, The Powder Coating Institute, located in Alexandria, VA. Journals such as the *Journal of Coatings Technology*, *Industrial Paint and Powder*, etc. now devote entire issues to the topic. Local, national, and international meetings are held to discuss the topic. The biennial trade show Powder Coating '92, held in Cincinnati, attracted over 4000 people, and 163 companies displayed their products. Powder coatings probably will not take over the coating industry, but they now are and continue to be important factors in the industry for the foreseeable future.

RADIATION CURING

Another new technology born in the late 1960s was radiation curing. It also showed great early promise and many problems—there were even unrealized problems at the beginning since no one really understood that some of the chemicals used were human sensitizers and strong irritants. Lack of knowledge in the scientific community about the hazards of acrylates resulted in some people becoming sensitized to these compounds. However, the idea of taking a liquid, low-viscosity, coating formulation, applying it to a substrate with conventional equipment, and having the coating essentially instantly converted into a solid, cross-linked film with very little or nil loss to the atmosphere was attractive.

Radiation curing involved the use of electron-beam or ultraviolet-light radiation. Free radicals were generated with ultraviolet light (photocure), and electrons were generated with electron beams. Acrylates and maleate polyesters/styrene were very rapidly polymerized in the presence of these active species. Because the reaction took place in thin films, the heat of reaction was readily dissipated and was not a problem to the technology. In the mid-to-late 1970s it was felt that this technology might capture only a percentage or two of the industrial coatings market.

Proponents of these essentially 100% solids systems refined the technology. Adaptation of existing equipment to the technology involved relatively simple, low-cost improvement when ultraviolet-light radiation was involved, and many conventional application techniques could be used. Most potential users insisted on the formulated products having low viscosity so that conventional equipment could be used. Such users were the driving force toward low-molecular-weight, reactive products. Innovators developed products that were quite safe to handle. A new branch of the technology that involved cycloaliphatic epoxides and photoinitiators that generated cationic species when photolyzed was begun at the end of decade.

Today, radiation-cure technology is considered a growth technology that is well established. It has developed to the point where it has its own technical society, RadTech International, located in Northbrook, IL, with large numbers of members and attendees at its meetings and exhibitions, which are held in North America, Europe, and Japan. Again, various journals have issues dedicated to the technology, and meetings or segments of meetings are held in various countries throughout the world. Radiation curing is currently a strong force in the market, and it is widely used to provide coatings for flooring, beverage cans (nonfood contact), electronics, plastics, paper, etc. It surely will also be a force in the future for as far ahead as we can see.

HIGH SOLIDS COATINGS

A third technology with its inception in the 1970s is high solids. Three factors provided the impetus for this technology and certainly had an effect on powder and radiation-cure coatings. First, the oil embargo during the mid-1970s caused the price of raw materials—including solvents—to increase significantly, and this was coupled with a significant scarcity of both petroleum-derived chemicals and fuel for energy purposes. Second, there was the energy cost involved in operating the huge ovens required to volatilize safely the large amount of solvent removed during the drying of the coatings. Not only were gas and oil costly, they were not readily available. High-solids, low-energy systems were developed in a feverish manner. Popular words in the industry at this time were "high solids" and "low energy cure."

Slowly the coating industry was coming to the realization that it might have to change—willingly or otherwise—from low solids and relatively easy to formulate systems to something new, be it powder coatings, radiation-cure coatings, water-borne coatings, or some other new technology. The third factor was related to concern about people and the environment. Everyone was becoming more and more conscious about the environment: in the workplace and the home as well as in a national and global geophysical sense. There was an awareness that solvents were being released into the atmosphere and into other parts of our ecological system, and that those solvents, though certainly not the only nor most important culprits, could have a long-term, deleterious effect on our environment and quality of life.

In addition to these factors, and very importantly, the government became strongly involved in regulation of the industry through the Environmental Protection Agency (EPA). The EPA is an agency that administers federal laws concerned with activities that affect the environment (details about the EPA and similar agencies are dealt with elsewhere in the manual). Governmental requirements, naive as some of them may have been at the outset, were established for the coating industry. For example, coatings were to contain no more than 20% volatile organic solvent. An industry that had been using formulations containing about 80 to 90% organic solvent and about 10 to 20% coating polymer was being asked (told) to change in a "quantum leap" manner. The industry was to develop formulations that significantly reduced the amount of organic solvent used and, of course, maintain ease of application, good protection, and aesthetically pleasing appearance. To term such a requirement "naive" may have been an understatement. The difficulty and impracticality of the requirement were realized, and over the years the standard has been modified. High(er) solids systems that contain more than 1 pound of polymer per pound of solvent are routinely used. Of course, this results in a markedly reduced volume of solvent that enters the atmosphere. Nonetheless, the change has been made and today almost all coatings are of the higher solids or 100% solids variety. Here, too, the industry discusses advances each year at The Water Borne and Higher Solids Coatings Conference that is cosponsored by the University of Southern Mississippi and the Southern Society and is held in the late winter of each year.

OTHER NEW COATING TECHNOLOGIES

Adjuncts to high-solids coating technology are the water-borne systems (though they may have predated organic-based systems) that require minimal cosolvent to achieve good appearance and properties, two-package coating systems that have relatively short pot lives, and water-borne emulsion or latex systems. The latter coatings are important

to the architectural coatings market, and today oil-base paints represent only a small fraction of the huge market for these commodity items. Latex-based paints have increased their solids, decreased volatile organic components, and are formulated with new thickening agents that have excellent flow characteristics. Even when the paint is applied by amateurs, spattering is almost unknown. This industry segment also is included in the above-mentioned symposium as well as at Lehigh University, which is well known for its efforts in the field of water-borne coating technology.

SOLVENTS

The area of solvent technology has undergone a number of changes during the past quarter of a century. The changes for the most part are associated with reduction of their health-hazard profiles and characteristics. Knowledge was developed or "rediscovered" about many solvents since the previous edition was published. This knowledge has led either to the demise or to "sharply" curtailed or restricted usage of what had been many commonly used solvents.

This same information was also responsible for innovation and has played an important role in development of new solvents that are less harmful to humans, animals, and the environment. The abbreviation MSDS (Material Safety Data Sheet) became well known for solvents and for other chemicals. Today these information sheets with safety data about materials are not only required for chemicals, they are used by people in laboratories and plants. It goes without saying that they should be required reading for anyone handling chemical compounds.

OTHER INNOVATIONS

The advent of new technology to produce functional and decorative coatings involved more than innovative organic chemistry. It also required innovative physical chemistry, material science, polymer science, and engineering. In addition to new chemicals and ways to use them, development of new application equipment and cure equipment was required. Conventional suction-feed spray guns and roll coaters could not be used for many of the new technologies. Powder coatings required development of methods of manufacture, of handling systems that could be quickly cleaned during a color change-over, of methods for placing a charge on the powder, of understanding and elimination of cage effects, of getting good wrap-around on other than flat substrates, of ways to remove fused powder from hangers and conveyors, and so on. Radiation-cure coatings required development of electron beam systems with improved safety features, of efficient ultraviolet light systems that could cure in other than line of sight, of low-viscosity chemicals with improved safety and health characteristics, and more. Water-borne systems had to deal with flash rusting, with minimizing cosolvents, with developing latexes that would quickly dry and fuse while maintaining qualities such as hardness, high gloss, and toughness. High solids required balances between molecular-weight, functional groups and their effects and viscosity, as well as between reactivity and shelf or pot life. It also required coating scientists to obtain high-quality finishes from the small molecules needed to achieve the low viscosity used for reasonable application characteristics at high-solids content.

Electronics also played an important role in the changes in coating technology and in the testing of coatings. During the period we are discussing, there has been a "Buck Rogerish" explosion in this industry. Many concepts and products related to such concepts that were considered amazing and with little likelihood of success in 1970 are realities today. Miniaturization technology has made printed circuit assemblies and semiconductors possible. Today, hand-held calculators are almost as powerful as the room-filling computers were in the early 1970s. Personal computers weren't even thought about in 1972. Robots and various forms of robotics have become useful tools in the 1990s. Application of electronics technology to a host of instruments, some of which are described in this manual, has vastly improved our ability to probe and otherwise examine and understand materials that are currently used, new materials as they are being developed, and final coatings in both an as-made and an aged condition. Both reliability and precision of tesing have been improved through new instruments.

Yet within this array of new test equipment that has been enabled through electronics and that allows quantitative results to be obtained in a reliable manner, there is still room for and a need for some of the simple, homey tests used for many years. Tests that are easy to apply and that require no elegant or complicated equipment are still desirable. Quickly drawing a nickel over a coating while applying downward pressure to the stroke almost immediately gives one a feeling for how well the coating is adhering to the substrate and to its toughness and formability. Such a test can be performed "on line" and by essentially anyone. Even interpretation of results is not difficult and is largely intuitive. Pencil hardness testing may vary from operator to operator, but one does not need to be a coatings scientist to quickly grasp what the test is measuring and to have a "feel" for a coating's hardness from the test. Solvent double rubs are easy to do. While the exact number of double rubs obtained may vary from individual to individual, the test still gives a quick understanding of the coating's thermoset character as well as the degree of cross-linking. Sharp impacts on the face or reverse side of a coated metal panel can quickly give an understanding about the impact and adhesion characteristics of the coating. These are four simple tests, but they can yield a great deal of understanding about a particular coating in a very short time. Other simple tests also exist.

Lest one get the wrong impression from the last few sentences, while these tests are useful, they certainly do not lead to the fundamental understanding that is very important to development of knowledge so necessary for new products. Sophisticated testing puts numbers on test results, probes deep into molecular achitecture, and allows both comparison of competitive products and the development of improved products. Sophisticated analyses also provide the understanding necessary to develop new chemicals and technology that will lead to improvements in existing products and to new products.

SUMMARY

Within the changed environment that has been described, the 13th edition of the *Paint Testing Manual* has, for the most part, become outdated—as was expected when it was compiled. Many of the methods described have changed, and the needs of the industry have also changed. The 14th edition reflects these changes. Even its title has been changed—to *Paint and Coating Testing Manual.* The collective effort of the many authors has resulted in a manual that has deemphasized, though certainly not eliminated, natural products, that provides a description of the regulations currently in force for the industry, and that discusses the main polymeric species, colorants, special pigments, extenders, and additives used in the industry today. The manual also deals with the analyses used to dissect and analyze a coating, the instruments used in the industry, and the products of the industry as well as how they are used and tested. Testing procedures for the most part are not detailed in the manual. Rather, the manual is a guide that will lead a coatings scientist to more in-depth treatises about the various topics and to test methods, procedures, and standards of ASTM and other national and international organizations.

Joseph V. Koleske
Editor

Part 1: Regulations

Regulation of Volatile Organic Compound Emissions from Paints and Coatings

1

by J. John Brezinski[1]

PRIOR TO THE 1960s the coatings industry enjoyed a somewhat predictable regulatory and economic environment. The paint formulator developing a solvent-based coating selected solvents on the basis of evaporation rate, solubility parameter, density, flammability, and, of course, cost. There was no apparent need to consider the relative photochemical reactivity of these materials, nor was there any appreciable incentive to reduce the solvent content of commercially acceptable coatings.

It was, of course, recognized that objectionable odors were released from some paints and coatings. Further, air emissions resulting from the evaporation of solvents during high-temperature processing of oils and resins caused occasional complaints from persons living near the coatings plant. The prevailing view of this period was summarized by Francis Scofield in his article in the 13th edition of the *Paint Testing Manual* entitled "Atmospheric Pollutants" [*1*].

> These "nuisance" types of pollution are a continuing problem but, in general, can be dealt with by dilution and dispersion of the objectionable materials to bring the concentration below a level that can be detected by the neighboring citizenry. Fortunately, most of the materials used by the paint industry are not toxic at concentrations significantly below the range at which they can be detected by the human nose, and sophisticated analytical procedures are rarely needed to deal with these "nuisance" problems.

Since the 1960s societal concern about health and the environment has increased appreciably. Actions taken by federal and state legislative bodies have resulted in a steady avalanche of new laws and associated regulations that affect virtually all industry. Among the new federal laws administered by the U.S. Environmental Protection Agency (EPA) that impact significantly on the coatings industry are those shown in Table 1. They are designed to control the emission of pollutants to air, to water, and to soil.

In addition, among the new federal standards administered by the Occupational Safety and Health Administration are those that require manufacturers—including those making paints and coatings—to evaluate the hazards of products they make and to provide appropriate safety information to employees and users through the Material Safety Data Sheet (MSDS) and product labels.

- Hazard Communication Standard (HCS), 1983
- Occupational Exposure to Hazardous Chemicals in Laboratories, 1990

[1]1046 College Circle, St. Albans, WV 25177.

TABLE 1—Federal environmental laws administered by the U.S. Environmental protection agency.

Law	Abbreviation
Clean Air Act, 1970	CAA
Amendments of 1977	CAAA-77
Amendments of 1990	CAAA-90
Clean Water Act of 1972 Amendments of 1977	CWA
Safe Drinking Water Act, 1974	SDWA
Toxic Substances Control Act, 1975	TSCA
Resource Conservation and Recovery Act, 1980	RCRA
Comprehensive Environmental Response Compensation and Liability Act, 1980	CERCLA (Superfund)
Superfund Amendments and Reauthorization Act, 1986	SARA
Title III, Emergency Planning and Community Right-to-Know, 1986	SARA, Title III

The discussion in this section will focus on the Clean Air Act and its amendments that, in the author's opinion, have had (and will continue to have) the greatest impact on coatings.

THE CLEAN AIR ACT AND ITS AMENDMENTS

California Smog

A precipitating factor influencing the basis for selection of solvents for coatings in the 1960s and early 1970s was the recognition that the emission of solvents from coatings to the atmosphere contributed to the growing "smog" problem in Southern California. The frequency of smog conditions in this area had increased steadily during the 1950s and 1960s as the number of automobiles, trucks, buses, and airplanes increased and as industrial development expanded with the accompanying growth of petroleum and chemical processing and power plant utilization.

The smog problem was (and is) most acute in the Los Angeles air basin, an area uniquely situated in a series of plains that originate in the high mountains to the east. The basin enjoys predominantly sunny days with cool moist air flowing with a light westerly wind most of the year. These factors cause a nearly permanent temperature inversion layer, trapping air emissions that combine to produce a persistent eye-irritating smog in the basin.

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In a presentation entitled "Solvent Restriction—Problem or Opportunity," Dr. John Gordon, then of the University of Missouri-Rolla, discussed the major sources of hydrocarbons and nitrogen oxides, which together in the presence of UV radiation react to produce oxidants and ozone, major components of smog [2].

$$HC + NO_x \frac{\text{Sunshine}}{\text{UV Radiation}} \text{Smog } (O_3)$$

Sources of NO_x: Flame of almost any kind, volcanoes, internal combustion engines, forest fires, cigarettes, boilers, space heaters.

Processes that Produce Hydrocarbons

- Petroleum production, refining, transport
- Internal combustion engines
- Natural processes—forests and plants (isoprene and terpenes)
- Surface coatings

A 1962 estimate of the contaminants discharged into the Los Angeles air during the summer period revealed that motor vehicles accounted for about 60%, while the use of organic solvents (for all purposes) accounted for about 18% of the organic gases. About one half of the organic solvent emitted was attributed to the coatings industry, chiefly to the use in paint and coatings. Approximately 66% of the NO_x released was assigned to gasoline (motor vehicle) combustion, while the combustion of fuels (energy supply) accounted for about 26% [1].

Based on the results of laboratory studies in "smog chambers," in which a mixture of a solvent and nitrogen oxide was exposed for 6 h to light approximately the intensity of noon sunlight, the solvents could be classified as "low" or "high" in photochemical reactivity related to the amount of peroxides and ozone produced. These studies formed the basis for the well-known Rule 66, an air pollution control regulation passed by the Los Angeles Air Pollution Control District. Rule 66 identifies an "approved" solvent as one that contains less than 20% by volume of specific chemicals and is further limited to certain combinations of these chemicals. Thus, approved solvents can contain no more than designated amounts of the combinations shown in Table 2.

In effect, Rule 66 promoted the use of specific solvents such as aliphatic and naphthenic hydrocarbons, alcohols, esters, normal ketones, chlorinated hydrocarbons (except trichloroethylene), and nitroparaffins. Rule 66, superseded in 1976 by Rule 442, Usage of Solvents, by the California South Coast Air Quality Management District, was subsequently adopted by various other state jurisdictions. Renewed interest has developed recently in the consideration of solvent photochemical reactivity in state, federal, and international programs related to air quality control.

TABLE 2—Rule 66—Limits of solvent categories in approved mixtures.*

5%	8%	20%
Hydrocarbons, alcohols, aldehydes, esters, ethers or ketones *having an olefinic or cycloolefinic unsaturation*	Aromatic hydrocarbons (W/8 C atoms)	Ethylbenzene, branched ketones, toluene, or trichloroethane

*Calculated as the percent by volume of the total solvent.

VOC Definition

The United States Environmental Protection Agency (EPA) was created in 1970 by Congress as part of a plan to consolidate several federal environmental activities. Studies directed by the EPA laboratories in Research Triangle Park, NC of the photochemical reactivity of materials in a laboratory smog chamber revealed that when organic materials and nitrogen oxide were irradiated for periods of up to 36 h, even those solvents considered acceptable under Rule 66 reacted to form peroxides and ozone. Only a few materials showed negligible photochemical reactivity, among which were: methane, ethane, methylene chloride, 1,1,1-trichloroethane, and fluorinated compounds. These studies, which were prompted in part by the passage of the Clean Air Act of 1970, led to the conclusion that most organic compounds emitted to the atmosphere contribute to the formation of ozone. On this basis, EPA adopted as a regulatory objective the limit of essentially all volatile organic compounds emitted to the atmosphere from all sources, including paint and coatings applications [3].

Regulatory Definition of VOC

The regulatory definition of volatile organic compounds (VOC) was revised by EPA in 1992. A part of this definition is as follows:

Section 51.100 Definitions[2]

Volatile organic compounds (VOC) means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.

(1) This includes any such organic compound other than the following, which have been determined to have negligible photochemical reactivity: methane; ethane; methylene chloride (dichloromethane); 1,1,1-trichloroethane (methyl chloroform); 1,1,1-trichloro-2,2,2-trifluoroethane (CFC-113); trichlorofluoromethane (CFC-11); dichlorodifluoromethane (CFC-12); chlorodifluoromethane (CFC-22); trifluoromethane (FC-23); 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114); chloropentafluoroethane (CFC-115); 1,1,1-trifluoro 2,2-dichloroethane (HCFC-123); 1,1,1,2-tetrafluoroethane (HF-134a); 1,1-dichloro 1-fluoroethane (HCFC-141b); 1-chloro 1,1-difluoroethane (HCFC-142b); 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124); pentafluoroethane (HFC-125); 1,1,2,2-tetrafluoroethane (HFC-134); 1,1,1-trifluoroethane (HFC-143a); 1,1-difluoroethane (HFC-152a); and perfluorocarbon compounds which fall into these classes:

(i) Cyclic, branched, or linear, completely fluorinated alkanes;

(ii) Cyclic, branched, or linear, completely fluorinated ethers with no unsaturations;

[2]40 Code of Federal Regulations (CFR) Part 51; Requirements for Preparation, Adoption and Submittal of Implementation Plans; Approval and Promulgation of Implementation Plans. *Federal Register*, Vol. 57, No. 22, 22 Feb. 1992, pp. 3941–3946.

(iii) Cyclic, branched, or linear, completely fluorinated tertiary amines with no unsaturations; and

(iv) Sulfur containing perfluorocarbons with no unsaturations and with sulfur bonds only to carbon and fluorine.

(2) For purposes of determining compliance with emissions limits. VOC will be measured by the test methods in the approved State implementation plan (SIP) or 40 CFR part 60, appendix A, as applicable. Where such a method also measures compounds with negligible photochemical reactivity, these neglibility-reactive compounds may be excluded as VOC if the amount of such compounds is accurately quantified and such exclusion is approved by the enforcement authority.

(3) As a precondition to excluding these compounds as VOC or at any time thereafter, the enforcement authority may require an owner or operator to provide monitoring or testing methods and results demonstrating, to the satisfaction of the enforcement authority, the amount of negligibly-reactive compounds in the source's emissions.

(4) For purposes of Federal enforcement for a specific source, the EPA will use the test methods specified in the applicable EPA-approved SIP in a permit issued pursuant to a program approved or promulgated under title V of the Act, or under 40 CFR part 51, subpart I or appendix S, or under 40 CFR parts 52 or 60. The EPA will not be bound by an State determination as to appropriate methods for testing or monitoring negligibly-reactive compounds if such determination is not reflected in any of the above provisions.

The Ozone Standard

The Clean Air Act of 1970 targeted six criteria pollutants for control: carbon monoxide, lead, nitrogen dioxide, ozone, particulates, and sulfur dioxide. Criteria pollutants are those for which criteria were issued by EPA. These documents include national ambient air quality standards (NAAQS)—levels that protect against adverse effects to health and to plants and materials [*4*]. Standards for ozone and nitrogen oxides are:

Ozone The ozone concentration in the atmosphere *cannot exceed 0.12 ppm as a daily maximum one-hour average more than once per year.*

Nitrogen Dioxide The nitrogen dioxide concentration in the atmosphere *cannot exceed 0.053 ppm as the annual arithmetic mean concentration.*

CONTROL OF VOC EMISSIONS FROM COATINGS

The Clean Air Act addressed air pollution eminating from both existing sources and that from future new plant construction or significant modification of existing sources. States with areas that did not comply with the ozone standard were given primary responsibility to develop appropriate regulations for existing sources to meet the time schedule for compliance specified by Congress. The Federal EPA was assigned oversight responsibility for the state programs that were described in "State Implementation Plans" (SIP).

Control Technique Guidelines

In 1977, the Agency issued the first of a series of guidance documents for the states related to various industrial coating operations or end-use categories. These documents, called "Control Technique Guidelines (CTG) Series, Control of Volatile Organic Emissions from Stationery Sources," include recommended VOC emission limits, based on EPA's assessment of Reasonably Available Control Technology (RACT): the limits are expressed as pounds of VOC per gallon of coating (minus water), as applied.

The Clean Air Act Amendments of 1977 directed that states had to revise their implementation plans for areas out of compliance with the national ozone standard. The revised SIPs were to include sufficient control of VOC emissions from stationery sources, such controls to incorporate the RACT limits for coatings operations for which a CTG was published.

The CTG documents relating to surface coatings operations issued through 1992 are shown in Table 3 with recommended limits for VOC content.

NEW SOURCE PERFORMANCE STANDARDS

The control of VOC emissions from new coatings plants and from significant modifications of existing plants was addressed by EPA in a series of New Source Performance Standards (NSPS), the first of which issued in 1980. These mandatory standards, which apply uniformly to all parts of the country, define the emission sources more narrowly and impose a tighter level of emission control than that for related existing sources. The VOC limits defined in the NSPS, expressed as kilograms of VOC per liter of applied solids, are based on the best demonstrated technology (BDT) for the specific coating operation.

The New Source Performance Standards for surface coatings operations issued through 1992 are shown in Table 4.

The emission limits in both the CTG and NSPS documents, in the majority of cases, focus on restricting the VOC content per unit of coating or of coating solids applied in the operation, rather than placing a ceiling on individual plant emissions. The responsibility for establishing emission limits for particular plants, if appropriate, was left to the states [*5*].

DETERMINATION OF VOC CONTENT

Federal Reference Method 24

The procedures specified by the federal EPA for testing paint products for compliance with VOC limits are described in Federal Reference Method 24 [*6*]. This standard employs several ASTM test standards, including those shown in Table 5.

Method D 2369 is a key procedure of Federal Method 24. Since 1980, several important revisions have been made in this standard to make it compatible with revisions in Method 24, including the addition in 1990 of instructions for testing multicomponent coatings and the deletion of sections dealing with testing at shorter times. The revised version of Federal

TABLE 3—VOC content limits in control technique guidelines (CTG) for surface coating operations.

Coatings Operation	CTG Date[a]	Allowable Limits[b]	Lb VOC/Gal Minus H_2O	Kg VOC/L Minus H_2O
Appliances, large	Dec., 1977		2.8	0.34
Auto and light duty trucks	May, 1977	Primer, electrodeposit	1.2	0.14
		Prime coat	1.9	0.23
		Guidecoat (surfacer)	2.8	0.34
		Topcoat	2.8	0.34
		Final repair	4.8	0.58
Cans	May, 1977	Sheet basecoat	2.8	0.34
		Interior body spray	4.2	0.51
		Side seam	5.5	0.66
		End seal compound	3.7	0.44
Fabric	May, 1977	Fabric coating	2.8	0.34
		Vinyl coating	3.8	0.45
Graphic arts—rotogravure and flexography	Dec., 1978	(Consult CTG or state regulations)		
Magnetic tape	See Paper coating			
Magnet wire	Dec., 1977	(Based on the use of an incinerator)	1.7	0.20
Metal coil	May, 1977	Prime and topcoat or single coat	2.6	0.31
Metal furniture	Dec., 1977		3.0	0.36
Miscellaneous metal parts and products	June, 1978	Air dry	3.5	0.42
		Clear coat	4.3	0.52
		Extreme performance	3.5	0.42
		Powder coatings	0.4	0.05
		All others	3.0	0.36
Paper, film and foil	May, 1977		2.9	0.35
Plastic parts for business machines	None			
Polymeric coatings of supporting substrates	None; may be considered fabric coating	...		
Pressure sensitive tapes and labels	See Paper coating	...		
Vinyl and urethane, flexible	Fabric: May 1977 and/or Graphic Arts Packaging Rotogravure, Dec. 1978	Vinyl	3.8	0.45
Wood paneling, flat	June, 1978	Printed interior panels: 6.0 lb/1000 sq. ft of surface coated		
		Natural finish plywood: 12.0 lb/1000 sq. ft of surface coated		
		Class II finishes 10.0 lb/1000 sq. ft of surface coated		

NOTE: The information presented in this table is not complete. Persons subject to emission control for any of the operations are advised to consult the state/local regulations for details.

[a]CTG documents are available from the National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

[b]Reasonably available control technology (RACT) limits recommended in CTG and, in most cases, adopted in state/local regulations.

Reference Method 24 is also included in the *ASTM Manual on Determination of Volatile Organic Compound (VOC) Content in Paints, Inks, and Related Coating Products*, 2nd ed., 1993 [7].

Substantial revisions during 1989–1991 were also made in ASTM D 3960, Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings, a standard developed in ASTM Subcommittee D01.21 to provide a guide for the calculation of VOC and to establish a base for the investigation in ASTM of the precision of VOC content determination. The definitions and symbols used in D 3960 are those adopted by the EPA and included in the Agency document "Procedures for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink and Other Coatings" that was published in 1984 [8].

The general expression for calculating VOC content in grams per liter of coating less water and exempt solvent specified in the EPA Control Technique Guidelines issued through 1991 is:

$$\text{VOC} = \frac{\begin{pmatrix}\text{Weight \% total volatiles}\\ \text{less water less}\\ \text{exempt solvent}\end{pmatrix}(\text{Density of coating})}{100\% - \begin{pmatrix}\text{Volume \%}\\ \text{water}\end{pmatrix} - \begin{pmatrix}\text{Volume \%}\\ \text{exempt solvent}\end{pmatrix}}$$

or

$$\text{VOC} = \frac{(W_o)(D_c)}{100\% - V_w - V_{ex}} = \frac{(W_v - W_w - W_{ex})(D_c)}{100\% - (W_w)(D_c/D_w) - (W_{ex})(D_c/D_{ex})} \quad (1)$$

where

VOC = VOC content in g/L of coating less water and exempt solvent,

W_o = weight % of organic volatiles = $W_v - W_w - W_{ex}$,

W_v = weight % of total volatiles = (100% − weight % nonvolatiles), (ASTM D 2369),

W_w = weight % of water (ASTM D 3792 or ASTM D 4017),

W_{ex} = weight % of exempt solvent (ASTM D 4457),

TABLE 4—VOC limits in New Source Performance (NSPS) for surface coatings operations.

Coatings Operation	NSPS Date[a]	Allowable Limits[b] Lb VOC/Gal Applied Solids	Kg VOC/L Applied Solids
Appliances, large	Oct., 1982	7.5	0.90
Auto and light duty trucks	Dec., 1980	Prime coat	
		1.3	0.16
		Guide coat	
		11.7	1.40
		Top coat	
		12.2	1.47
Cans (beverage cans only)	Aug., 1983	Exterior base	
		2.4	0.29
		Clear base coat	
		3.8	0.46
		Inside spray	
		7.4	0.89
Fabric (coating)	See Polymeric coating of supporting substrate		
Graphic arts—rotogravure and flexography	Rotogravure only Nov., 1982	Consult NSPS document	
Magnetic tape	Oct., 1988	1.7	0.2
		Consult NSPS	
Magnet wire	None	...	...
Metal coil	Nov., 1982	w/o emission control device	
		2.3	0.28
		With emission control device	
		1.2	0.15
Metal furniture	Oct., 1982; Apr., 1985	7.5	0.90
Miscellaneous metal parts and products	None	...	...
Plastic parts for business machines	Jan., 1988	Prime and color coat	
		12.52	1.5
		Texture and touch-up	
		19.2	2.3
Polymeric coatings of supporting substrates	Sept., 1989	90% control from process: Consult NSPS	
Pressure sensitive tapes	Oct., 1983	1.67	0.20
Vinyl and urethane, flexible	June, 1984	8.3	1.0
Wood paneling, flat	None	...	...

NOTE: The information presented in this table is not complete. Persons subject to emission control for any of the operations are advised to consult the specific language of the referenced documents and state and local regulations.

[a]NSPS documents are available from the National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, VA 22161.

[b]Best demonstrated technology (BDT) emission limits established as NSPS standards. In the NSPS, the limits are expressed as kilograms of VOC per liter of applied solids.

TABLE 5—ASTM standards referenced in Federal Reference Method 24.

ASTM Method	Test Method for—
D 2369-81	Volatile Content of Coatings
D 1475-60	Density of Paint, Varnish, Lacquer, and Related Products
D 3792-79	Water Content of Waterborne Paints by Direct Injection into a Gas Chromatograph
D 4017-81	Water in Paints and Paint Materials by Karl Fischer Method
D 4457-85	Analysis of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph

V_w = volume % of water = $(W_w)(D_c/D_w)$,
V_{ex} = volume % of exempt solvent = $(W_{ex})(D_c/D_{ex})$,
D_c = density of coating at 25°C in g/L (ASTM D 1475),
D_w = density of water at 25°C in g/L = 0.997×10^3, and
D_{ex} = density of exempt solvent at 25°C in g/L (ASTM D 1475).

To convert from g/L to lb/gal, multiply the result (VOC content) by 8.345×10^{-3} (lb/gal)/g/L). To convert g/L to kg/L, divide the result by 10^3.

The general expression for VOC content defined in terms of the mass of VOC per unit volume of coating solids applied as specified in the EPA New Source Performance Standards is

$$\mathrm{VOC}_m = \frac{(W_v - W_w - W_{ex})D_c}{V_n} \tag{2}$$

where

VOC_m = VOC content in g/L of coating solids, and

V_n = Volume % nonvolatile content of the liquid coating, ASTM D 2697.[3]

The EPA would have preferred to limit volatile organic compound emissions in the Control Technique Guidelines on the basis of the unit volume of coating solids applied. The adoption in the 1970s of Eq 1, in which VOC content is defined as mass per unit volume of coating less water and less exempt solvents, was necessary as no acceptable consensus procedure was available for determining the volume percent nonvolatile content. In a presentation in Copenhagen in 1990, James C. Berry of U.S. EPA stated: "Though certainly less than ideal, the major attraction is that the expression permits the determination of compliance from the analysis of a coating sample obtained during a plant inspection. In the simplest case, these units require only one volumetric and one gravimetric measurement" [5].

Studies and discussions in ASTM Subcommittee D01.21 that led to the modification and improvements of ASTM standards referenced in Federal Method 24 and in ASTM Practice D 3960 were conducted with the cooperation of EPA personnel of the Office of Air Quality Standards Development at Research Triangle Park, NC.

OTHER VOC-RELATED METHODS AND STUDIES

ASTM development activity on other VOC-related standards has expanded significantly since 1980. Many of the standards listed in this section have not been approved by the Federal EPA for use in demonstration of compliance with VOC emission control regulations. Use of any of these standards to demonstrate compliance should be coordinated with appropriate regulatory agencies. Among the new standards developed or in process of development are the following:

Standards Specific to the Automobile Industry

- D 5087 Test Method for Determining the Amount of Volatile Organic Compounds (VOC) Released from Solvent-Borne Automotive Coatings and Available for Removal in a VOC Control Device (Abatement)
- D 5066 Practice for the Determination of the Transfer Efficiency Under Production Conditions for Spray Application of Automotive Paints—Weight Basis
- D 5009 Test Method for Evaluating and Comparing Transfer Efficiency Under Laboratory Conditions

These standards were developed with the cooperation of representatives from automotive coating suppliers and the Motor Vehicle Manufacturers Association. Method D 5009 was derived from a study of transfer efficiency conducted for the U.S. Environmental Protection Agency [9].

Masonry Treatments

- D 5095 Test Method for Determination of the Nonvolatile Content in Silanes, Siloxanes, and Silane-Siloxane Blends Used in Masonry Water-Repellent Treatments.[4]

In this standard, a catalyst is added prior to the bake cycle to simulate the catalytic effect provided by masonry during actual application of the water-repellent treatment.

Aerosol Spray Paints

- D 5200 Test Method for Determination of Weight Percent Volatile Content of Solvent-borne Paints in Aerosol Cans
- D 5325 Test Method for the Determination of Weight Percent Volatile Content of Water-borne Aerosol Paints

These standards were developed for potential use related to proposed regulations in California to limit the level of volatile organic material in aerosol paints.

General Application Standards

- D 5201 Practice for Calculating Formulation Physical Constants of Liquid Paints and Coatings

The calculation of various physical constants directly from the paint formulation is a common practice in industry. ASTM D 5201 describes procedures for the calculation of *formulation* weight solids, volume solids, solvent content, and density of liquid paint based on formulation data (not analytical laboratory determinations). The values obtained may not be acceptable for demonstrating regulatory compliance.

- D 5286 Test Method for Determination of Transfer Efficiency Under General Production Conditions for Spray Application of Paints

This standard, a modification of Practice D 5066 developed for use in the automobile industry, describes conditions for determining transfer efficiency under production conditions applicable to spray application of miscellaneous parts.

- D 5327 Practice for Evaluating and Comparing Transfer Efficiency under General Laboratory Conditions

Practice D 5327 provides a useful guide for general research studies related to transfer efficiency. The general approach employed is derived from that developed in Method D 5009 except that D 5327 employs a fixed rather than moving spray station.

- Revision of D 2697, Test Method for Volume Nonvolatile Matter in Clear or Pigmented Coatings: Use of the Helium Gas Pycnometer (Under Study)

The use of the helium gas pycnometer provides a quick, reliable approach to the determination of the dry coating density, a critical parameter in the calculation of volume percent nonvolatile content.

- Direct Measurement of Volatile Organic Material in Water-Reducible Coatings (Under Study)

Federal EPA funds supported the preliminary investigation of this novel approach to the "direct" gravimetric determina-

[3]EPA Reference Method 24 does not include an analytical method for determining V_n, but states that the value be calculated from the coating manufacturer's formulation.

[4]This standard has been accepted by the Federal EPA for use in the determination of the VOC of silane- and siloxane-based coatings: Letter, Gary McAllister, EPA, to H. Smith, NJ Dept. of Environmental Protection, 25 March 1992.

tion of volatile organic content of waterborne coatings [*10*]. The method involves collecting, on activated charcoal in weighed tubes, the organic effluent evolved on heating a paint specimen for 1 h at 110°C while purging the reaction vessel with dry nitrogen. Methanol is not captured on the charcoal.

- D 5403 Test Method for Volatile Content of Radiation Curable Materials

The test methods in D 5403 determine the weight percent volatile content of paint, coatings, and inks that are designed to be cured by exposure to ultraviolet light or to a beam of accelerated electrons. After radiation cure, the specimens are baked at 110 ± 5°C for 60 min.

Inks

- D 5328 Volatile Organic Compound (VOC40) Content of Non-Heatset Paste Printing Ink Systems at 40°C

This standard is patterned, in part, after Method 30 of California's Bay Area Air Pollution Control District in which the specimen is baked for 1 h at 40°C. D 5328 is applicable to paste printing inks and vehicles that dry primarily by absorption, polymerization, or related means without the application of heat.

Supplementary Information

Further information about the development, significance, and limitations of these VOC-related ASTM standards as well as about the use of ASTM standards for the demonstration of compliance with VOC emission control regulations is available in the ASTM *Manual on Determination of Volatile Organic Compounds in Paints, Inks, and Related Coating Products* [*7*]. Attachments in the second edition of this manual include the 1992 revision of Federal Reference Number 24 and a publication from EPA's Emission Standards Division titled "Procedure for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink and Other Coatings" [*8*]. Included in the latter publication are "VOC Data Sheets" applicable to coatings "as supplied" by the manufacturer and for coatings "as applied" by the user. The form used for "as supplied" coatings is patterned after a recommendation of the National Paint and Coatings Association.

CLEAN AIR ACT AMENDMENTS OF 1990

The Clean Air Act Amendments of 1990 defined a comprehensive long-term approach "to achieve and maintain a healthy environment while supporting a strong and sustainable economic growth and sound energy policy."[5] A major impetus for these amendments was the continued inability of a number of heavily populated urban areas to meet the requirements of the national ambient air quality standards for ozone and carbon monoxide.

Among the specific issues addressed in the Act are: control of ozone in the atmosphere; control of hazardous air pollutants; reduction of acid rain; and the protection of ozone in the stratosphere.

Features of the Act that will impact most on the coatings industry include:

Title I—Ozone Control in the Atmosphere

Title I specifically directs EPA to develop control technique guidelines and maximum achievable control technology (MACT) standards for aerospace coatings and for shipbuilding coatings and repair. EPA was also directed to prepare new control technique guidelines for additional coatings uses that include:

- autobody refinishing
- plastic parts (business machines)
- plastic parts (others)
- offset lithography
- wood furniture

In addition, EPA plans to promulgate national rules to control VOC emissions from architectural and industrial maintenance coatings and from traffic paints. Solvent emission from consumer and commercial products, including that from aerosols, are currently under study, and regulation of this broad category of products is planned. In the development of these rules, negotiated rulemaking may be employed, a process bringing together representatives of EPA, industry, the states, and environmentalist groups to negotiate the content of a proposed rule.

In CAAA-90, ozone nonattainment areas are placed in five classifications based on the mid-1991 ozone level (Table 6), and compliance with the national ozone standard by specific years is mandated in the law.

Increasingly strict provisions, including further reduction of VOC emissions, will be imposed on areas, the magnitude to be related to the severity of the ozone problem. Depending on the area classification, several or all of the following will be required:

- Increased monitoring and more accurate VOC and NO_2 emission inventory
- Revision of state implementation plans to incorporate RACT limits from previous and future CTGs for all major stationery sources
- New source review and permits for new or modified stationery sources
- Reduced emission threshold levels for the definition of major stationery sources, ranging between 10 tons/year for severe classification areas to 100 for marginal or moderate areas

TABLE 6—Clean air act amendments—1990 ozone nonattainment area classifications.

Classification	Design Value (Ozone Level)	Years to Achieve Compliance, year
Marginal	0.121–0.138	3 (1993)
Moderate	0.138–0.160	6 (1996)
Serious	0.160–0.180	9 (1999)
Severe	0.180–0.280	15 (2005)
Extreme[a]	0.280 and above	20 (2010)

[a]Only the Los Angeles area is in this classification.

[5]U.S. EPA Office of Air and Radiation, "Implementation Principles for the Clean Air Amendments of 1990."

- Higher VOC emission offset requirements for new or modified sources

Title III—Air Toxics Program

Under Title III, EPA is directed to evaluate and control the emission of hazardous air pollutants (HAPS). 189 products are identified in the Act, and EPA has the authority to delete or add additional products to this list. Industry groups may petition EPA to delist products.

Among the materials included on the initial HAP list that are used in paints and coatings are those shown in Table 7.

The control of emissions of hazardous air pollutants is to be achieved through the promulgation of emission standards for source categories and subcategories that emit these products. The initial list of categories of sources published by EPA (57FR31576, 16 July 1992) included under *Surface Coating Processes* those processes for which a CTG or national rule has been issued or is planned. Also included is the *Manufacture of Paints, Coatings and Adhesives.* A draft timetable for regulating the categories of sources of hazardous air pollutants was published by EPA in 1992 (57FR44147, 24 Sept. 1992). By the end of 1994 emission standards were due for the following surface coating processes: magnetic tapes, printing/publishing, shipbuilding and ship repair, and wood furniture.

The Agency was required to publish emission limits based on maximum achievable control technology (MACT) for 40 of these categories by the end of 1992, with MACT limits to be identified for the remaining categories by 2000. The Act directs that the health impact and economic factors be considered in defining appropriate MACT limits. Further, by the end of 1995 sufficient categories and subcategories must be listed to ensure that 90% of the area sources that emit the 30 most hazardous air pollutants are subjected to regulation.

TABLE 7—Clean air act amendments—1990 selected hazardous air pollutants used in paints and coatings.

ORGANIC MATERIALS
Bis (2-ethylhexyl phthalate)
Dibutyl phthalate
Diethanolamine
Dimethyl formamide
Dimethyl phthalate
Ethylene glycol
Formaldehyde
Glycol ethers (ethylene oxide-based)
Methanol
1,1,1-trichloroethane (methyl chloroform)[a]
Methylene chloride[a]
Methyl ethyl ketone[a]
Methyl isobutyl ketone[a]
2-nitropropane
Styrene
Toluene[a]
Xylenes[a]
INORGANIC AND OTHER
Ammonia
Antimony compounds
Cadmium compounds[a]
Chromium compounds[a]
Cobalt compounds
Lead compounds[a]
Mercury compounds[a]

[a]Materials included in the EPA/Industry 33/50 Project, a voluntary industry initiative to reduce the total release and transfer of 17 targeted chemicals by one third by the end of 1992 and by one half by the end of 1995 (using 1988 as a baseline year).

Title V—State Operating Permit Program

The state operating permit program is considered by EPA as a cornerstone of the CAAA-90 amendments designed to ensure that the ozone nonattainment areas meet compliance deadlines. This program will impact on many previously unregulated coatings manufacturers and users. The final rule re the operating permit program was issued in 1992 (57FR32250, 21 July 1992).

The operating permit program has been called the "air pollution equivalent" of the NPDES permit program of the Clean Water Act, under which operating permits are required of sources that discharge pollutants to water. In the program under Title V, all federal and state air pollution rules and regulations will be consolidated under a single document wherein the states are given authority to monitor and enforce the regulations. Sufficient funds will be available to the states from a minimum annual fee of $25 per ton for each regulated pollutant emitted, the fee to be assessed against all major sources.

Major sources required to have state operating permits include those that emit 10 tons or more per year of a single regulated hazardous air pollutant or 25 tons per year of a combination of hazardous air pollutants. These pollutants include those materials for which a national emission standard (NESHAP) has been established. Under Title V of CAAA-90, and the final rule on operating permit programs, EPA is to approve (or disapprove) state permit programs within one year of receipt; the major sources must apply for the five-year permit within one year of the EPA's approval of the state program, and all permits must be issued and be legally binding by the end of 1997. Under the rule, states have the option of exempting all nonmajor sources, with some exceptions, from requiring a permit for five years after the state permit program is approved by EPA.

The characterization of a major source in ozone nonattainment areas is also based on the amount of volatile organic compounds emitted annually. The threshold amount is related to the area classification and sources in ozone nonattainment areas that emit above the designated amount of VOC shown in Table 8 are identified as major sources. These limits vary between 10 tons/year for the "extreme" classification to 100 tons/year for the "marginal or moderate" classification.

For ozone transport regions (e.g., one is established in the Northeast), a threshold limit of 50 tons/year of VOC emission applies.

TABLE 8—Clean air act amendments—1990 major source identification based on VOC emissions: limits for area classifications.

Ozone Nonattainment Area Classification	VOC Emission Limit, tons/year
Marginal or moderate	100
Serious	50
Severe	25
Extreme	10

TABLE 9—Code of federal regulations subchapter topics.

Subchapter	Subject	Parts
C	Air Programs	50–87
	New Source Performance Standards	60
D	Water Programs	104–149
I	Solid Waste	240–281
J	Superfund/Right-to-Know	300–372
N	Effluent Guidelines and Standards	401–471
R	Toxic Substances Control Act	700–799

TABLE 10—Control technique guidelines and surface coating operations reference documents.

EPA Document Reference		Coating Operation
EPA-450/2-77-008	Vol. II	Auto and light duty trucks
		Cans
		Fabric
		Metal Coil
		Paper, film, and foil
EPA-450/2-77-032	Vol. III	Metal furniture
EPA-450/2-77-033	Vol. IV	Magnet wire
EPA-450/2-77-034	Vol. V	Appliances, large
EPA-450/2-78-015	Vol. VI	Miscellaneous metal parts and products
EPA-450/2-78-032	Vol. VII	Wood paneling, flat
EPA-450/2-78-033	Vol. VIII	Graphic arts—rotogravure and flexography
		Vinyl and urethane, flexible

Title VI—Stratospheric Ozone Protection

The most significant feature of the program to protect ozone in the stratosphere is the staged phaseout of 1,1,1-trichloroethane, a material widely used in coatings and classified as a "VOC-exempt" solvent by the EPA. Production (and use) will be reduced in increments (from the 1989 amount) beginning in 1993 to a 50% level for the period 1996–1999, then to the 20% level for the period 2000–2001, after which the use of the material will be prohibited.

Title VII—Enforcement

EPA is granted broad new authority to impose penalties and substantial fines for various actions including: violations of the State Implementation Plan; violation of some of the operating permit provisions; and false statements in records, monitoring data, and reports. Also included are provisions for field citations by inspectors.

Scenario for the 1990s

CAAA-90 and the myriad of new federal and state regulations associated with implementation of this comprehensive law that will issue during the 1990s will have a major impact on the coatings industry. Among the many uncertainties are the nature and level of MACT limits to be defined for essentially all coating operations; the level of new or stricter VOC

TABLE 11—Regional offices, U.S. Environmental Protection Agency.

Region	States	Address
1	Connecticut, Maine, Massachusetts, New Hampshire, Rhode Island, Vermont	J. F. Kennedy Federal Bldg. Room 2203, Boston, MA 02203 Phone (617) 565-3715
2	New Jersey, New York, Puerto Rico, Virgin Islands	26 Federal Plaza New York, NY 10278 Phone (212) 264-2515
3	Delaware, Maryland, Pennsylvania, Virginia, West Virginia, District of Columbia	841 Chestnut St. Philadelphia, PA 19107 Phone (800) 438-2474
4	Alabama, Florida, Georgia, Kentucky, Mississippi, North Carolina, South Carolina, Tennessee	345 Courtland St. NE Atlanta, GA 30365 Phone (800) 282-0239 in GA (800) 241-1754 in other Region 4 states
5	Illinois, Indiana, Michigan, Minnesota, Ohio, Wisconsin	230 S. Dearborn St. Chicago, IL 60604 Phone (800) 572-2515 in IL (800) 621-8431 in other Region 5 states
6	Arkansas, Louisiana, New Mexico, Oklahoma, Texas	1445 Ross Ave. 12th Floor, Suite 1200 Dallas, TX 75202 Phone (214) 655-2200
7	Iowa, Kansas, Missouri, Nebraska	726 Minnesota Ave. Kansas City, KS 66101 Phone (913) 236-2803
8	Colorado, Montana, North Dakota, South Dakota, Utah, Wyoming	999 18th St. Suite 500 Denver, CO 80202 Phone (800) 759-4372
9	American Somoa, Arizona, Nevada, Hawaii, Guam, California	215 Fremont St. San Francisco, CA 94105 Phone (415) 974-8076
10	Alaska, Idaho, Oregon, Washington	1200 6th Ave. Seattle, WA 98101 Phone (206) 442-5810

emission limits for coating operations; and the time, manpower, and cost associated with complying with the many new regulations associated with the amendments.

As did the decades of the 1970s and 1980s, the 1990s will pose a continuing challenge to raw material suppliers to develop and provide environmentally acceptable materials as well as to paint formulators to develop new or modified coatings with reduced VOC content. Additionally, increased attention to the improvement of coating processes and to the use of abatement equipment for emission control during the application of coatings is expected.

REGULATION INFORMATION

Published Sources

Federal environmental regulations, including those promulgated under the Clean Air Act, are published in the *Code of Federal Regulations* (CFR), a series of books that are generally available in major libraries and law libraries. These regulations as well as those of related state and local codes are also obtainable from the associated regulatory offices.

Regulations of particular interest to the coatings industry can be found in subchapters of the *Code of Federal Regulations* (Table 9).

The Federal Control Technique Guidelines for coating operations are not included in the CFR, but are available from the National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, VA 22161. CTG documents through 1991 are included in the EPA publications listed in Table 10.

Proposed regulations are published by the EPA in the *Federal Register.* Typically, a public (written) comment period of 30 to 90 days on the proposals is allowed, and often a public hearing is scheduled at which oral comments can be presented. The comments received are considered by the Agency in the development of a final regulation that is published in the *Federal Register* together with the regulation compliance date.

Information Sources

Questions relating to the interpretation, applicability, and compliance to air quality regulations may be addressed to the U.S. EPA regional offices or to the specific state regulating body responsible for air quality control.

The U.S. Environmental Protection Agency has established ten regional offices, each responsible for several states (Table 11).

Among the industry organizations that provide information to their membership about pending regulations and guidance on compliance with finalized regulations are Chemical Manufacturers Association (CMA), National Paint and Coatings Association (NPCA), Dry Colour Manufacturer's Association (DCMA), and Chemical Specialty Manufacturers Association (CSMA). Several coatings journals publish excerpts from regulations and summary reviews.

REFERENCES

[*1*] Scofield, F. in *Paint Testing Manual,* 13th ed., American Society for Testing and Materials, Philadelphia, 1972, p. 413.

[*2*] Gordon, J., "Solvent Restriction, Problem or Opportunity," presentation to the Chicago Coatings Society, 13 Nov. 1978.

[*3*] EPA Policy Statement, Recommended Policy on Control of Volatile Organic Compounds, *Federal Register,* 8 July 1977.

[*4*] "Glossary for Air Pollution Control of Industrial Coating Operations," EPA-450/3-83-013R, Environmental Protection Agency, Washington, DC, December 1983.

[*5*] Berry, J. C., U.S. EPA, "Control of Volatile Organic Compound (VOC) Emissions from Painting Operations in the United States," presentation at the International Symposium on Paint and the Environment, Copenhagen, 12–14 Nov. 1990.

[*6*] *Code of Federal Regulations,* Vol. 40, Subchapter C., Part 60, Appendix A; Amendments in a Rule published in the *Federal Register,* Vol. 57, No. 133, 10 July 1992, pp. 30654–30656.

[*7*] *Manual on Determination of Volatile Organic Compounds in Paints, Inks, and Related Coating Products, ASTM Manual Series, MNL4,* 1989, 2nd ed., 1993.

[*8*] *Procedures for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink and Other Coatings,* EPA-450/3-84-019, Environmental Protection Agency, Washington, DC, December 1984.

[*9*] *Development of Proposed Standard Test Method for Spray Painting Transfer Efficiency,* Vols. I and II, EPA Publication Nos. EPA-600/2-88-026a and EPA-600/2-88-026b, Environmental Protection Agency, Research Triangle Park, NC.

[*10*] *Method Development for Measuring the VOC Content of Water-Based Coatings,* EPA Contract No. 68D90055, Work Assignments No. 28 and 40, Environmental Protection Agency, Research Triangle Park, NC.

Part 2: Naturally Occurring Materials

2

Bituminous Coatings

by Ben J. Carlozzo[1]

INTRODUCTION

General Overview

IN THE UNITED STATES, the terms "bituminous" and "asphaltic" are often used interchangeably. In Europe, bitumen refers to the mixture of heavy hydrocarbons, free of inorganic impurities. Asphalt is often considered the impure form of the generic material [*1*]. For our purposes, the ASTM definitions will be used.

ASTM Definitions of Terms Relating to Roofing, Waterproofing, and Bituminous Materials (D 1079-87a) [*2*] defines bitumen as either ". . .(1) a class of amorphous black or dark colored (solid, semi-solid, or viscous) cementitious substances, natural or manufactured, composed principally of high molecular weight hydrocarbons, soluble in carbon disulfide, and found in asphalts, tars, pitches and asphaltites; or, (2) a generic term used to denote any material composed principally of bitumen."

Asphalt is similarly defined as ". . .a dark brown to black cementitious material in which the predominating constituents are bitumens which occur in nature or are obtained in petroleum processing." While the term has historically implied the natural deposits (the Trinidad Lake asphalts on the Island of Trinidad or the Bermudez Lake, Venezuela asphalts), most asphalt used in the United States today for coatings applications is from petroleum processing [*3*].

History and Background of Bitumens

As one of man's oldest engineering materials, the adhesive and waterproofing properties of bitumen have been known since the earliest days of civilization. The area between the Tigris and Euphrates rivers in Iraq, long believed to be "the cradle of civilization," contains the earliest deposits of asphalt and heavy liquid petroleum. Early historical and biblical accounts tell of the use of asphalt in shipbuilding and foundation mortars. The Egyptians were known to have used asphalt in the mummification process; in fact, the part-Persian word for asphalt, "mumiya," is where our word "mummy" is derived [*4*].

The first asphalts produced in the United States were derived from California crude oils in the late 19th century. A straight run distillation, often without steam, was able to produce a good-quality material suitable for paving work. Most of this material was competing with foreign imports from the Lake Trinidad region on the Isle of Trinidad off the north coast of South America. In the early 20th century, Mexican asphalt obtained from Mexican crude oil was used extensively in the eastern United States and gained a reputation as a high-grade standard paving bitumen.

Today, asphalts are found throughout the world in several natural deposits of soft bituminous material or as hard, glassy, black bitumen associated with certain rock formations or impregnating various limestone or sandstone-type formations. Additionally, asphalts are derived from colloidally dispersed asphalt hydrocarbons in crude petroleum. This leads to the classification of bitumens into two classes: (1) natural asphalts (bitumens) and (2) artificial or oil asphalts (petroleum asphalts).

The purity of bituminous materials is generally related to the degree that they are soluble in certain organic solvents. For years, the degree of solubility in carbon disulfide (CS_2) has been a typical method for determining the purity of natural asphalts. ASTM Test Method for Bitumen Content (D 4-86) formalizes this procedure with CS_2 solubility as the primary screening test. Most oil asphalts are generally greater than 99% soluble in CS_2.

The natural asphalts can be further classified by the geographical region of their origin, as well as the extent to which impurities are present, for example, Trinidad, refined, of approximately 50 to 57% bitumen; Cuban, refined, of 80 to 90% purity; Bermudez, refined, of 85 to 92% purity; and various rock asphalts, i.e., limestone, sandstone, tar sands, etc., with varying degrees of bitumen content.

A separate class of natural bitumens are the asphaltites. These are also called the solid bitumens and are asphalts without impurities (silts, clays, salts, etc.), although their degree of CS_2 solubility varies. Examples of these materials are Gilsonite, grahamite, glance pitch, or manjak, as well as harder materials that show no softening point, such as the pyrobitumens. The most important of these for coatings applications is Gilsonite.

Artificial bitumens have been classified into three major groups [*5*]:

1. Oil or petroleum asphalts are soft to hard asphalts of high solubility in carbon disulfide (more than 99%) and are classed as pure bitumens. They are obtained from the vacuum or steam distillation of crude oils containing high asphalt content. The distillation concentrates the colloidally dispersed asphalt into the "still bottoms" or "residuum" and is often a solid material.

[1]Mameco International, Inc., Cleveland, OH.

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Precipitation methods are also used to recover asphalt from raw lubricating oils. This de-asphalting operation uses propane or other low-boiling hydrocarbons. The materials produced are the so-called asphaltic resins, with the hard, high asphaltene asphalts as the precipitate. Variations are made by controlling the propane stream.

Oxidized or "blown" asphalts are obtained by blowing air at high temperatures through soft or liquid petroleum residues. This procedure can take semi-asphaltic materials of low purity and produce considerable amounts of bitumen. The resulting material is harder, with a higher softening point.

2. "Cracked" asphalts are also petroleum derivatives, but are obtained from by-products in oil-cracking processes. Residues are distilled to produce asphalt. They are variable in composition and may contain a certain amount of uncracked paraffinic material. These materials represent asphaltic hydrocarbons approximately intermediate in aromaticity between oil asphalts and the completely aromatic, highly condensed bitumens found in coal tars, water-gas tars, coal carbonization tars, and their pitches.
3. Coal tar, water-gas tars, and their pitches are derived from tars. ASTM D 1079 defines tar as ". . .a brown or black bituminous material, liquid or semi-solid in consistency, in which the predominating constituents are bitumens obtained . . . from the processing of coal, petroleum, oil-shale, wood, or other organic materials." The "free carbon" content, or other benzene insoluble matter, distinguishes coal tar from the asphaltites and oil asphalts. The latter are devoid of free carbon. Coal tars and their products are not included in the category of asphalt.

In the early 1960s, approximately 70% of all oil asphalts were consumed by the road-paving industries with 20% used in roofing. The solid bitumens and asphaltites of natural origin found their greatest consumption in lacquer, paint, and electrical insulation. Today, the paving industry is still the largest user of these materials, but the scope and area of specialty coatings has broadened considerably. In recent years, asphalts and other bitumens have become increasingly important as the cost of other natural and synthetic binders has continued to escalate. Their ability to act as adhesives with excellent moisture vapor transmission (MVT) properties continues to result in new and varied uses.

Coating Types

The types of asphaltic or bituminous coatings available can be classified, in a large part, by the industry of use. Industries considered are:

1. The paints and coatings industry, where bituminous coatings have been used to protect metal from the effects of water and oxygen degradation.
2. The roofing industry, where asphalt coatings are used extensively to weatherproof buildings.
3. The construction industries, where concrete and mortar are waterproofed.
4. The paving industry, where the adhesive properties of asphalt as binder is put to good use in roads.

Specialty Paints and Coatings

Asphalt, coal tar, and other bitumens have been used in several specialty areas in the paint and coatings industry. The predominate use has been in the area of pipe coatings and automotive under-body coatings, although containment coatings are fast becoming a sizable market.

In pipe coatings, the base bitumen forms an inter-penetrating network with a thermosetting resin to form an impervious barrier to groundwater and the effects of catastrophic rusting. On deep buried pipes or those set in concrete, the cost associated with the use of an expensive binder is offset by the large replacement costs involved. The thermoset resins most frequently used have been the epoxides. The bitumens used in these coatings have generally been the coal tars and pitches. This was primarily due to the compatibility of these highly aromatic materials with epoxy resins, as well as the ease of working with a liquid material. The final film hardness is derived from the cross-linked epoxy network.

There has been a growing concern with the toxicity of highly aromatic systems. The result has been that trade sales and light industrial coatings have moved away from coal tar or its pitches. Recently, the asphaltites and oil asphalts have been used in these types of coatings. The trend has been to use softer asphalts. Some form of compatibilizer has also been necessary to make these lower aromatic-content systems stable.

In automotive under-body rustproofing, bituminous coatings have found extensive use. These materials are modified with rubbery materials to give flexible coatings with excellent adhesion to metal parts. Many years ago, the predominant bitumen in use had been coal tar. Today, with the move away from highly aromatic products, petroleum asphalts are generally used. To use the harder bitumens such as asphaltites and petroleum asphalts, plasticizers such as di-octyl phthalate or butyl benzyl phthalate are required to soften and liquify the bitumen. Aromatic processing oils have also been used for this purpose. Natural and synthetic waxes are added to prevent chipping from road debris.

Given the severe penalties associated with contamination of groundwater, chemical and moisture-resistant coatings for containment dikes are being used more and more in the chemical process industry. Most state and local regulations require the use of a containment wall around every storage tank that may potentially rupture and contaminate the water table.

Coatings for this application have included coal tar epoxies and coal tar resinous systems. Gilsonite-based resinous coatings have been widely used and, depending on the chemical nature of the contained material, petroleum asphalt urethanes and epoxides are available.

Additional areas where bitumens have shown applicability as specialty coatings have included the areas of sealing soil to minimize water penetration (pond liners, seepage control for levees and dams, and hazardous waste containment) as well as sound deadening on sheet metal and binding other bituminous materials such as coal or lignite for pelletization.

Roof Coatings

In roof coatings, bitumens have been important raw materials since the turn of the century. Today, many commercial roofing systems use some form of asphalt or chemically mod-

ified asphalt in their construction. The application of an asphalt or polymer-modified hot melt asphaltic material, followed by the application of a reinforcing membrane, is the basic construction of a modern built-up-roof (BUR).

In some markets, the current industry trend has been away from the use of hot melt coatings, where a roofing kettle that heats the materials up to 450°F (232°C) to reach their application viscosity is required, and toward cold-applied systems. Here, the asphalt is usually modified with solvents, fillers, and thixotropes as well as various additives to result in a formulation that can be applied at ambient temperatures with good flow properties and that which will subsequently dry or cure into a weatherproofing membrane.

In these coatings, volatile solvents are varied to control cure times. In general, the solvents are either mineral spirits or naphthas. While asbestos was long a preferred additive for thixotropy and reinforcement, the hazards of working with and removing old installations with asbestos-containing materials have driven the products toward asbestos-free roofing materials. This has led to the use of cellulose, synthetic, and glass fibers as a partial replacement for asbestos. Bentonite and attapulgite clays are then used to obtain the required thixotropy. Today, there are still a significant number of manufacturers that continue to use asbestos in their formulations.

The asphalt portion of these coatings usually consists of materials referred to as cutbacks. Various solvents are used to cut (solubilize) the asphalt, depending on the cure times required. The solvent predominantly used today is mineral spirits, with a flash point (tag closed cup) of 104°F (40°C). Faster evaporating versions of these cutbacks have been used as primers for better substrate adhesion. These materials generally use faster aromatic solvents, including toluene, xylene, and the aromatic naphthas. The asphalt content varies from 30 to 70% by weight.

The preceding materials, while they can, in the strictest sense, be considered coatings, are actually closer to adhesives in performance; that is, these coatings are applied to hold the reinforcing membranes together. Although the last coat applied may be a flood coat of the adhesive coating, the roof is usually not left this way. Weathering characteristics are significantly improved when these roofs are gravel surfaced. This graveled surface blocks harmful ultraviolet (UV) radiation and serves to improve the fire resistance. The most common roof gravels are river-washed gravel, crushed stone, granite, and blast-furnace slag recovered from the iron ore reduction process and composed of silicates and aluminosilicates of lime [*6*]. Other materials, also available for this purpose, include a variety of small, colored roofing granules, similar to those used on shingles.

From 400 to 600 lb (181 to 272 kg) of river-washed gravel per 100 ft^2 (9.29 m^2) of roof is used, or, if weight considerations are important, 50 to 60 lb (22.68 to 27.2 kg) of the smaller roofing granules can be used. The bituminous coating is then an adhesive for these gravels.

Due to weight limitations on existing roofs and costs associated with roof tear-offs and subsequent reroofing, current philosophy is to maintain the existing roof. When physically possible, restoration instead of replacement is very cost effective. This requires the use of coatings whose purpose is to repair damage to the roof and re-establish or maintain the weather-tight seal. After the repairs are complete, a reflective coating may be applied to act as an ultra-violet (UV) barrier and thermal reflector, or additional gravel added. Several different types of coatings have been available for each of these purposes.

Asphalt cutbacks and emulsions are the primary coating used for restoration. They are applied in heavy applications of 40 to 80 mil thick. This allows the coating to cover minor surface defects that are present on the old roof. Splits and cracks can be repaired by using these materials with either fiberglass or polyester reinforcements. A final application gives a reasonably water-tight monolithic appearance.

Asphalt emulsions consist of two types. In one, the water is dispersed in the asphalt external phase. In the other, the asphalt is dispersed in a water external phase. The first are called water-in-oil (W/O) emulsions. The later are oil-in-water (O/W) emulsions. Roofing emulsions are predominately water-in-oil emulsions. The oil-in-water emulsions are more widely used in the paving industry and will be discussed in more detail in that section.

The water-in-oil emulsions are produced from finely powdered clays, which can act as dispersants for the water. Dispersing agents of this type show some affinity for water or are sufficiently hygroscopic to hold water and bring it into dispersion in the asphalt. The bentonite clays form extremely colloidal gelatinous mixtures and pastes with water and result in asphalt dispersions of very small particle size. These smooth buttery emulsions are very stable and can be fibered for reinforcement and modified with latex resins to obtain a degree of elasticity. Most commercial products are unmodified and yield a final coating possessing all the properties of a gel asphalt after evaporation of the water. Several books are available which offer greater detail in the area of emulsion technology [*7–9*].

Asphalt emulsions can be left untop-coated, but are frequently coated with reflective topcoats to help control roof top temperatures. For several years, the major type of coatings for this application have been solvent-borne aluminum pigmented bituminous coatings. A wide variety of bitumens have been used, including asphalt, asphaltite, tar, and pitch. Their viscosity has generally been low with moderate levels of volatile solvents present. Most of the solvent-based aluminum bitumen paints in use today are asphalt vehicles made from petroleum asphalt cutbacks. The predominate solvent has been mineral spirits. The pigment used has generally been a leafing grade of aluminum paste. It is reported that some early formulations used cumerone indene resin to improve the leafing characteristics and act as an anti-bronzing agent. A level of 2 lb (0.91 kg) of aluminum paste per gallon of paint is typical in these coatings [*10*].

With the recent increase in environmental legislation and an increased awareness of health issues, alternatives to these solvent-borne coatings are beginning to find their place in the market. Specifically, asphalt emulsions of various solids are being used in conjunction with new aluminum pigment technology which allows the manufacture of relatively stable waterborne versions [*11,12*]. These materials generally consist of petroleum asphalt emulsions that use organophosphate-treated leafing-aluminum pastes. The phosphate passivates the aluminum, giving it more stability on storage. The solids of such coatings vary from 25 to 50% by weight. Additional

modification similar to other emulsion systems is also used in these coatings.

Newer technologies to stabilize aluminum pigments in water have recently been introduced. Chemically bound chrome is used to passivate the aluminum [*13*]. While quite expensive, these products are finding use in the automotive industry. As their cost decreases, perhaps they will be available for the waterborne bituminous aluminum market.

Other technologies exist that are nonbituminous in composition. These coatings include elastomeric acrylic latexes, solvent and waterborne urethanes, epoxides, and alkyds. These are usually pigmented with either titanium dioxide (TiO_2) or aluminum pastes to give thermally reflective coatings. These types of coatings will be discussed elsewhere in this manual.

Waterproofing Membranes

Bitumen-modified waterproofing membranes are used extensively in the construction industry. The most common substrate is poured or cast concrete or mortared "cinder block." Prestressed concrete in the foundations, walls, and roof decks of high-rise buildings is also a suitable candidate for these membranes. In the home construction and repair industries, cinder block foundations and concrete footers are commonly waterproofed with bitumen-modified polymeric coatings.

The bitumen of interest in these markets has predominately been coal tar pitch and petroleum asphalts. Waterproofing membranes are generally composed of bitumen in an elastomeric polymer matrix. The aromatic polyurethanes are frequently used for this purpose.

In coating structural steel and steel reinforcement bars, coal tar epoxies have been extensively used. Their composition and purpose is similar to that of pipe coatings used for the prevention of underground corrosion. Their composition can be modified to conform to a particular steel coatings application.

As in other markets, the use of aromatic coal tars is slowly being replaced by safer soft petroleum asphalts. Environmental issues aside, higher tech systems are beginning to be seen. Other types of coatings for rebar in the last five years have included fused epoxy powder coatings systems and polyethylene dip coated systems. While much more expensive than bitumen-modified systems, their improved performance have made them of interest.

Coatings for Paving

The paving industry is probably the oldest using bitumen and its coatings. Asphalt cutbacks have also been known as "road oils." For years these solvent cut materials were used to seal roads as well as coat aggregates for application to the road surface. Today, hot asphalt or cutback is used to prime new paving as well as to repair damaged or worn areas.

Today, most road coating uses asphalt emulsions. These are generally chemically stabilized emulsions. The emulsion is prepared beforehand and mixed with aggregate on site and is referred to as *chip* and *seal*. Hot asphalt is not required in this application, making it much easier than the use of hot mix paving, where the asphalt is heated to melting before application. In paving, oil-in-water emulsions predominate.

The oil-in-water emulsions are formed from the action of a chemical emulsifier, either anionic, cationic, or nonionic in nature. The anionic and cationic emulsifiers form an emulsion in which the dispersed phase shows a definite charge. These emulsions are said to "break" upon contact with a charged aggregate, yielding the exclusion of one phase from the other. The speed of break can be modified, yielding rapid, medium, or slow setting emulsions. The cationic versions are preferred because the coating formed does not re-emulsify. With anionic emulsifiers, break occurs when emulsions destabilize due to water loss on drying. One disadvantage of this is the possibility of re-emulsification in the early stages of cure. Once the coating has dried, water is no longer a problem.

Paving sealers are used to protect new or old asphalt driveways or parking lots. The sealers are generally coal tar in nature due to good resistance to gas and oil. Asphalt sealers can also be used, but they must be latex or polymer modified to improve solvent resistance.

Other types of bituminous coatings used in the paving industry include slurry seals and micro surfacing, which uses latex or polymer-modified asphalts with fine aggregate filler as a surface treatment for repair of minor damage to roads. Coal tar is not used in this application because the resulting coating is too slippery. Tack coats consisting of asphalt cutbacks are also used when one layer of asphalt needs to be adhered to another.

IDENTIFICATION OF BITUMINOUS MATERIALS

This section will catalogue several test methods currently available through ASTM for characterization of bituminous paints and coatings. Many of these methods are familiar to the coatings chemist as standard paint-related tests found in Volumes 6.01 through 6.04 of the *Annual Book of ASTM Standards*. Several others are under the jurisdiction of Committee D 8 on Roofing, Waterproofing, and Bituminous Materials. These methods appear in Volume 4.04 of the *Annual Book of ASTM Standards*.

Tests on Bituminous Materials

The following test methods are used to differentiate one type of bitumen from another. They also can distinguish mixtures of bitumens and their purity. As bitumens are considered pseudo-plastic materials, with no true melt point, softening point and penetration are the two major tests routinely performed to identify differences within grades of the different bitumen classes. Viscosities at elevated temperatures are also very important with several instruments and their methods listed.

In earlier editions of this manual, several tests were described that were in common use in 1972. Among the tests described were the solubility of bitumens in carbon disulfide (CS_2) to identify the purity of a bitumen sample, since by definition only CS_2 soluble matter is bitumen. Also listed were tests to determine the presence of asphalt and tar in suspected mixtures (the Oliensis Spot Test and the characteristics of bituminous samples dispersed in solvent). Today, these have been incorporated into the *Annual Book of ASTM Standards* and will not be described in detail.

On this note, it is important to point out that each industry that uses bitumens has tended to develop their own series of common pertinent tests over the years. Today most of the pertinent tests have been incorporated as ASTM standards. In addition to ASTM, other organizations have tried to compile these tests for their members' use. The Asphalt Institute, an international, nonprofit organization sponsored by members of the petroleum asphalt industry, also publishes a handbook that has evolved over the past 50 years as the standard reference work in the field of asphalt technology and construction, especially in the paving industry [*14*]. This reference book cites both ASTM test methods and, where applicable, American Association of State Highway and Transportation Officials (AASHTO) counterparts to these methods. A large part of the manual is devoted to practical how-to information about how to use asphalt, as well as comprehensive data on asphalt technology, and is highly recommended.

General

D 4-86 Test Method for Bitumen Content

D 5-86 Test Method for Penetration of Bituminous Materials

D 36-86 Test Method for Softening Point of Bitumen (Ring and-Ball apparatus)

D 70-82 Test Method for Specific Gravity and Density of Semi-Solid Bituminous Materials

D 88-81 Test Method For Saybolt Viscosity

D 92-90 Test Method For Flash and Fire Points by Cleveland Open Cup

D 95-83 Test Method for Water in Petroleum Products and Bituminous Materials by Distillation

D 140-88 Practice for Sampling Bituminous Materials

D 529-90 Test Method for Accelerated Weathering Test Conditions and Procedures for Bituminous Materials

D 1079-87 Definitions of Terms Relating to Roofing, Waterproofing, and Bituminous Materials

D 1669-89 Method for Preparation of Test Panels for Accelerated and Outdoor Weathering of Bituminous Materials

D 1670-90 Test Method for Failure End Point in Accelerated and Outdoor Weathering of Bituminous Materials

D 4798-88 Test Method for Accelerated Weathering Test Conditions and Procedures for Bituminous Materials (Xenon-Arc Method)

D 4799-88 Test Method for Accelerated Weathering Test Conditions and Procedures for Bituminous Materials (Fluorescent UV and Condensation Method)

D 4989-90 Test Method for the Apparent Viscosity Flow of Roofing Bitumens Using the Parallel Plate Plastometer

E 96-90 Test Methods for Water Vapor Transmission of Materials

E 102-81 Test Method for Saybolt Furol Viscosity of Bituminous Materials at High Temperatures

E 108-90 Method for Fire tests of Roof Coverings

Specifications and Test Methods for Asphalt

D 71-84 Test Method for Relative Density of Solid Pitch and Asphalt

D 312-89 Specification for Asphalt Used in Roofing

D 449-89 Specification for Asphalt Used in Dampproofing and Waterproofing

D 1328-86 Test Method for Staining Properties of Asphalt

D 1370-84 Test Method for Contact Compatibility Between Asphaltic Materials (Oliensis Test)

D 1856-79 Test Method for Recovery of Asphalt from Solution by Abson Method

D 2042-81 Test Method for Solubility of Asphalt Materials in Trichloroethylene

D 2521-76 Specification for Asphalt Used in Canal, Ditch, and Pond Lining

D 3461-85 Test Method for Softening Point of Asphalts and Pitches (Mettler Cup-and-Ball Method)

D 4402-87 Test Method for Viscosity Determinations of Unfilled Asphalts Using the Brookfield Thermosel Apparatus

Specification and Test Methods for Coal Tar, Pitches, and Highly Cracked Petroleum Products

D 61-75 Test Method for Softening Point of Pitches (Cube-in-Water Method)

D 450-78 Specification for Coal Tar Pitch Used in Roofing, Dampproofing, and Waterproofing

D 2318-86 Test Method for Quinoline-Insoluble (QI) Content of Tar and Pitch

D 2319-76 Test Method for Softening Point of Pitch (Cube-in-Air Method)

D 2320-87 Test Method for Density (Specific Gravity) of Solid Pitch (Pycnometer Method)

D 2415-66 Test Method for Ash in Coal Tar and Pitch

D 2416-84 Test Method for Coking Value of Tar and Pitch (Modified Conradson)

D 2569-89 Test Method for Distillation of Pitch

D 2764-81 Test Method for Dimethylformamide-Insoluble (DMF-I) Content of Tar and Pitch

D 2962-71 Method for Calculating Volume-Temperature Correction for Coal-Tar Pitches

D 3104-87 Test Method for Softening Point of Pitches (Mettler Softening Point Method)

D 4072-81 Test Method for Toluene-Insoluble (TI) Content of Tar and Pitch

D 4312-89 Test Method for Toluene-Insoluble (TI) Content of Tar and Pitch (Short Method)

D 4616-87 Test Method for Microscopical Analysis by Reflected Light and Determination of Mesophase in a Pitch

D 4715-87 Test Method for Coking Value of Tar and Pitch (Alcan)

D 4746-87 Test Method for Determination of Quinoline Insoluble (QI) Content in Tar and Pitch by Pressure Filtration

D 4892-89 Test Method for Density of Solid Pitch (Helium Pycnometer Method)

D 4893-89 Test Method for Determination of Pitch Volatility

D 5018-89 Test Method for Shear Viscosity of Coal Tar and Petroleum Pitches

TESTS AND SPECIFICATIONS FOR COATINGS

General Tests for Coatings

Several of the test methods familiar to the industrial paints and coatings chemist can also be used to characterize the performance and physical properties of bituminous coatings. The following methods can all be found in Volumes 6.01 through 6.04 of the *Annual Book of ASTM Standards*.

Tests and Specifications

B 117-90 Method of Salt Spray (Fog) Testing

D 522-88 Test Methods for Mandrel Bend Test of Attached Organic Coatings

D 555-89 Guide for Testing Drying Oils

D 562-81 Test Method for Consistency of Paints Using the Stormer Viscometer

D 609-90 Practice for Preparation of Cold-Rolled Steel Panels for Testing Paint, Varnish, Conversion Coatings, and Related Coating Products

D 610-85 Method for Evaluating Degree of Rusting on Painted Steel Surfaces

D 662-85 Test Method for Evaluating Degree of Erosion of Exterior Paints

D 714-87 Method for Evaluating Degree of Blistering of Paints

D 1212-85 Test Methods for Measurement of Wet Film Thickness of Organic Coatings

D 1474-85 Test Methods for the Indentation Hardness of Organic Coatings

D 1475-90 Test Method for Density of Paint, Varnish, Lacquer, and Related Products

D 1540-82 Test Method for Effect of Chemical Agents on Organic Finishes Used in the Transportation Industry

D 1542-60 Test Method for Qualitative Detection of Rosin in Varnishes

D 1640-83 Test Methods for Drying, Curing, or Film Formation of Organic Coatings at Room Temperature

D 1644-88 Test Methods for Nonvolatile Content of Varnishes

D 1654-79 Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments

D 1849-80 Test Method for Package Stability of Paint

D 2243-90 Test Method for Freeze-Thaw Resistance of Water-Borne Paints

D 2247-87 Practice for Testing Water Resistance of Coatings in 100% Relative Humidity

D 2369-90 Test Methods for Volatile Content of Coatings

D 2370-82 Test Method for Tensile Properties of Organic Coatings

D 2832-83 Guide for Determining Volatile and Nonvolatile Content of Paint and Related Coatings

D 3170-87 Test Method for Chip Resistance of Coatings

D 3359-90 Test Methods for Measuring Adhesion by Tape Test

D 3960-90 Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings

G 6-88 Test Method for Abrasion Resistance of Pipeline Coatings

Solvent-Thinned or Cut-Back Coatings

General

D 255-70 Method for Steam Distillation of Bituminous Protective Coatings

D 402-76 Test Method for Distillation of Cut-Back Asphaltic (Bituminous) Products

D 529-90 Test Method for Accelerated Weathering Test Conditions and Procedures for Bituminous Materials (Carbon-Arc Method)

D 3105-90 Index of Methods for Testing Elastomeric and Plastomeric Roofing and Waterproofing Materials

Roof Coatings

D 41-85 Specification for Asphalt Primer Used in Roofing and Waterproofing

D 43-73 Specification for Creosote Primer Used in Roofing, Dampproofing and Waterproofing

D 1227-87 Specification for Emulsified Asphalt Used as a Protective Coating For Built-Up Roofing

D 2823-90 Specification for Asphalt Roof Coatings

D 2824-85 Specification for Aluminum-Pigmented Asphalt Roof Coatings

D 3805-85 Practice for Application of Aluminum-Pigmented Asphalt Roof Coating

D 4479-85 Specification for Asphalt Roof Coatings—Asbestos Free

D 5076-90 Test Method for Measuring Voids in Roofing and Waterproofing Membranes

Waterproofing Membranes

D 41-85 Specification for Asphalt Primer Used in Roofing, Dampproofing and Waterproofing

D 43-73 Specification for Creosote Primer Used in Roofing, Dampproofing and Waterproofing

D 5076-90 Test Method for Measuring Voids in Roofing and Waterproofing Membranes

Paving Sealers

D 3320-90 Specification for Emulsified Coal Tar Pitch (Mineral Colloid Type)

D 3423-84 Practice for Application of Emulsified Coal Tar Pitch (Mineral Colloid Type)

D 4866-88 Performance Specification for Coal Tar Pitch Emulsion Pavement Sealer Mix Formulations Containing Mineral Aggregates and Optional Polymeric Admixtures

Specialty Coatings

D 41-85 Specification for Asphalt Primer Used in Roofing and Waterproofing

D 43-73 Specification for Creosote Primer Used in Roofing, Dampproofing and Waterproofing

D 1187-82 Specification for Asphalt-Base Emulsions for Use as Protective Coatings for Metal

Emulsion Coatings

General

D 466-42 Method of Testing Films Deposited from Bituminous Emulsions

D 529-90 Practice for Accelerated Weathering Test Conditions and Procedures for Bituminous Materials (Carbon-Arc Method)

D 1187-82 Test Method for Asphalt-Base Emulsions for Use as Protective Coatings for Metal

D 2939-78 Method for Testing Emulsified Bitumens Used as Protective Coatings

Clay Stabilized Emulsions

D 1227-87 Specification for Emulsified Asphalt Used as a Protective Coating For Built-Up Roofing

D 2963-78 Test Method for Testing Flow Table Consistency of Clay-Stabilized Asphalt Emulsions

D 3320-90 Specification for Emulsified Coal Tar Pitch (Mineral Colloid Type)

Anionic Emulsions

D 1227-87 Specification for Emulsified Asphalt Used as a Protective Coating For Built-Up Roofing

Non-Ionic Emulsions

D 1227-87 Specification for Emulsified Asphalt Used as a Protective Coating For Built-Up Roofing

Cationic Emulsions

D 1227-87 Specification for Emulsified Asphalt Used as a Protective Coating For Built-Up Roofing

Resin Modified Bituminous Coatings

Synthetic Resins

D 3468-90 Specification for Liquid-Applied Neoprene and Chlorosulfonated Polyethylene used in Roofing and Waterproofing

CONCLUSION

Bituminous coatings are still used extensively today. The waterproofing and adhesive properties, coupled with the relatively inexpensive costs for most bituminous materials, continue to drive their use in many diverse industrial applications. The preceding information will give the reader an understanding of the chemistry and uses of bituminous coatings in industry and a realization that even several thousand years after their discovery and first use the usage of these bituminous raw materials as an engineering raw material is still growing.

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[*11*] Williams, J. E., U.S. Patent No. 4,565,716, 1986.

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3

Cellulose Esters

by L. G. Curtis[1]

CELLULOSE ESTERS ARE THE reaction product of combining organic acids and acid anhydrides with the hydroxyl groups found on the anhydroglucose repeating units of a cellulose molecule. The esterification of the cellulose with the acids and anhydrides occurs quite rapidly and if allowed to proceed to completion, forms a triester with each of the anhydroglucose units, which contain three hydroxyl groups. Because the triester is of little practical use, hydrolysis is necessary to restore desired levels of hydroxyl content, which affects various properties of the cellulose ester such as solubility and compatibility with other coating polymers.

PRODUCTION OF CELLULOSE ESTERS

For the production of coating-grade cellulose esters, three organic acids and anhydrides are used, either separately or in combination with each other. Cellulose acetate is the simplest cellulose ester since only acetic acid and acetic anhydride are used in the esterification reaction. If two different organic acids and anhydrides are used simultaneously, the resultant product is referred to as a mixed ester. Examples of mixed cellulose esters are cellulose acetate butyrate and cellulose acetate propionate.

In addition to esterification and hydrolysis, several subsequent processing steps are required in the manufacture of cellulose esters including filtration, precipitation, washing, dewatering, drying, and screening. The final product is a dry, free-flowing powder in most instances, although other physical forms can be produced. Unlike cellulose nitrate, organic esters of cellulose are low in flammability and present no handling hazards.

TYPES OF CELLULOSE ESTERS

Several types of cellulose esters are commercially available, including cellulose acetate, cellulose acetate propionate, and cellulose acetate butyrate. Other esters of lesser commercial value are produced, but are not suited for coating applications. Table 1 shows the types of cellulose esters commercially available. Cellulose acetate butyrate is the most commonly used organic cellulose ester for coating applications, and there is an almost infinite number of types that can be produced because of the acetylbutyryl combinations that are possible. Hydroxyl content and molecular weight possibilities expand this range even further.

FACTORS AFFECTING PERFORMANCE OF CELLULOSE ESTERS IN COATINGS

Performance properties of cellulose acetate buytrate are affected by the chemical composition and the viscosity of the ester. As butyryl increases, solubility, compatibility, flexibility, diluent tolerance, and moisture resistance are increased. Lower butyryl levels are associated with decreased water tolerance, grease resistance, hardness, and increased melting range. As the hydroxyl content of cellulose acetate butyrate varies, several characteristics are also affected. Below 1% hydroxyl, solubility in common coatings type solvents is limited but improves as the hydroxyl increases. At levels around 5%, solubility in lower molecular weight alcohols occurs. At higher hydroxyl levels, reactivity increases, providing cross-linking capability with amino and isocyanate resins. However, in noncross-linking systems, higher levels decrease moisture resistance due to increased hydrophilicity.

The viscosity of cellulose esters also influences physical properties of the ester as well as coatings formulated with them. Increasing the viscosity of a particular ester by increasing the molecular weight slightly lowers its solubility and compatibility with other resins, but does not affect hardness and density. Generally, toughness and flexibility are improved with increased molecular weight and viscosity.

APPLICATIONS FOR CELLULOSE ESTERS IN COATINGS

Protective and decorative coatings for various substrates can be formulated either as air-dry lacquer systems or as converting or curing types often referred to as cross-linked enamels. In many such coatings, cellulose esters are included as either a modifying resin to impart a specific property to the coating or to function as the primary film-forming resin in the formulation. Both types of coatings can be applied over a variety of substrates ranging from paper products to automobiles. Some areas in which cellulose esters are used include automotive OEM and refinish, wood furniture coatings, leather coatings, printing inks, plastic coatings, aircraft coatings, cable lacquers, and various fabric coatings. Cellulose esters are used in coatings to impart such properties as rapid-

[1]Principal Technical Representative, Eastman Chemical Company, Building 230, Kingsport, TN 37662.

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TABLE 1—Commercial cellulose esters (Eastman Chemical Company).

Type	Viscosity,[a] s	Acetyl,[b] %	Propionyl, %	Butyryl, %	Hydroxyl, %	Melting Range, °C
			Cellulose Acetate			
CA-394-60S	60.00	39.5	...	...	4.0	240–260
CA-398-3	3.00	39.8	...	...	3.5	230–250
CA-398-6	6.00	39.8	...	...	3.5	230–250
CA-398-10	10.00	39.8	...	...	...	230–250
CA-398-30	30.00	39.8	...	...	...	230–250
			Cellulose Acetate Propionate			
CAP-482-0.5	0.50	2.5	45.0	...	2.6	188–210
CAP-482-20	20.00	2.5	46.0	...	1.8	188–210
CAP-504-0.2	0.20	0.6	42.5	...	5.0	188–210
			Cellulose Acetate Butyrate			
CAB-171-15S	15.00	29.5	...	16.0	1.1	230–240
CAB-321-0.1	0.10	18.5	...	31.2	1.3	165–175
CAB-381-0.1	0.10	13.5	...	37.0	1.3	155–165
CAB-381-0.5	0.50	13.5	...	37.0	1.3	155–165
CAB-381-2	2.00	13.5	...	37.0	1.3	175–185
CAB-381-20BP	2.20	14.5	...	36.0	1.8	175–185
CAB-381-20	20.00	13.5	...	36.0	1.8	195–205
CAB-381-20BP	16.00	15.5	...	36.0	0.8	185–195
CAB-500-5	5.00	4.0	...	51.0	1.0	165–175
CAB-531-1	1.90	3.0	...	50.0	1.7	135–150
CAB-551-0.01	0.01	2.0	...	52.0	1.8	130–140
CAB-551-0.2	0.20	2.0	...	52.0	1.5	127–142
CAB-553-0.4	0.40	2.0	...	46.0	4.8	150–160

[a]ASTM Test Method for Cellulose Acetate Proprionate and Cellulose Acetate Butyrate (Formula A) (D 817) and Test Methods for Viscosity of Cellulose Derivatives by Ball-Drop Method (D 1343).
[b]ASTM D 817.

drying, pigment control, viscosity control, film toughness, and polishability.

TESTING OF CELLULOSE ACETATE

Cellulose acetate is tested by the manufacturer in accordance with ASTM Test Methods for Cellulose Acetates (D 871), which covers color and haze, combined acetyl, free acidity, heat stability, hydroxyl content, intrinsic viscosity, moisture content, sulfur or sulfate content, and solution viscosity. Coatings manufacturers usually restrict their testing to viscosity of the ester, solubility and appearance, and color and haze.

Viscosity

Viscosity measurement of cellulose acetate is carried out in accordance with ASTM Test Methods for Viscosity of Cellulose Derivatives by Ball-Drop Method (D 1343) based on the ball drop or falling ball principle. A precision Hoeppler viscometer is used in most viscosity determinations with results reported in ASTM seconds. Formulations for viscosity determination are shown in Table 2.

Solubility and Appearance

The solubility and appearance test is performed to determine the possible presence of insoluble gel particles, fibers, flock, or other contaminants, using solutions prepared for viscosity testing. The material to be tested is added to 16 oz. (454 g) French square bottles and visually compared to a reference standard.

TABLE 2—Solutions for viscosity measurement of cellulose acetate, cellulose acetate propionate, and cellulose acetate butyrate.

Cellulose ester	20[a]	20[a]	20[b]	15[c]	20[a]	10[c]
Acetone[d]	70	80	...	...	...	...
Acetone/water, 96/94	...	...	...	...	80	...
Ethyl alcohol[e]	8	...	8	8.5	...	...
Methyl alcohol[f]	...	...	...	...	...	9
Methylene chloride[g]	...	...	72	76.5	...	81
Typical Solution Densities, g per mL at 25°C	0.85	0.86	1.25	1.23	0.86	1.24

[a]For cellulose acetate having a max of 40.5% acetyl and for most mixed esters having less than about 40% acetyl and more than about 8% propionyl or butyryl.
[b]For cellulose acetate having 40.5 to 42.7% acetyl and for most of the commercial cellulose acetate propionate and acetate butyrates.
[c]For cellulose acetate having 42.7 to 44.8% acetyl and for most of the commercial cellulose acetate propionate and acetate butyrates; particularly good for esters containing more than 40% acetyl.
[d]Acetone (99.4 ± 0.1%) containing 0.3 to 0.5% water and under 0.3% ethyl alcohol.
[e]Ethyl alcohol (95% by volume). Formulas 2B, 3A, or 3O denatured ethyl alcohol may be used.
[f]Methyl alcohol (sp gr 20/20°C = 0.785 to 0.795).
[g]Methylene chloride having a boiling range of 39.2 to 40.0°C and less than 0.001% acidity calculated as HCL.

Color and Haze

The same solutions used for ASTM viscosity and solubility and appearance testing are normally used for color and haze measurements. The solution is transferred to a special 33-mm-square cell, and the analysis is performed with a Gardner Model XL-385 colorimeter. Light passes through the solution, and the primary yellowness index and primary haze values are simultaneously displayed by the instrument. Secondary color, based on platinum/cobalt standards, and secondary haze, based on scattered light from a monodisperse

polystyrene latex suspension, are calculated. APHA color and ASTM haze are predicted from the secondary values.

TESTING OF CELLULOSE ACETATE PROPIONATE AND CELLULOSE ACETATE BUTYRATE

ASTM Test Method for Cellulose Acetate Propionate and Cellulose Acetate Butyrate (D 817) contains the following tests: acetyl and propionyl or butyryl contents; apparent acetyl content; free acidity; ash; color and haze, heat stability, hydroxyl content; moisture content; sulfur content; and viscosity. Usually color and haze and viscosity are the only tests run by the coatings manufacturer. The test methods are the same as those used in the testing of cellulose acetate.

4

Drying Oils

by Joseph V. Koleske[1]

DRYING OILS REPRESENT A SMALL PORTION of the huge fats and oils industry.[2] In 1987 there were 81 000 metric tons (~178 million pounds) of drying oils consumed in the United States [*1*]. With an expected annual average growth rate of 2.6%, there should have been 92 000 metric tons consumed in 1992. Such consumption represents about 3% of the total nonfood fats and oils market and about 1% of the combined food and nonfood fats and oils national market. The industry is very mature with relatively little growth expected. Within this industry, whose growth is about the same as the population growth of the United States, drying oil consumption, though relatively very small, has the highest expected growth rate over the above five-year period. The paint and coating industry's need for drying oils is in an overall decline along with other end use markets, such as binders for hardboard, sealants, plasticizers, linoleum, and core oils. Drying oils used in paints and coatings are being replaced with oil-free, synthetic, petroleum-derived oligomeric and polymeric binders carried in a variety of media or in a neat manner. The printing ink market is the only one expected to have small growth in the area of drying oils.

Usually in the fats and oils industry, products solid at room temperature are referred to as fats, and products liquid at room temperature are termed oils. Often times the terms "fats" and "oils" are used interchangeably within the industry. Drying oils, except for fish oil, are of vegetable origin.

Chemically, drying oils are water-insoluble, unsaturated glycerides of long chain fatty acids with the generalized structure

$$\begin{array}{l} CH_2{-}O{-}OC{-}R_a \\ | \\ CH{-}O{-}OC{-}R_b \\ | \\ CH_2{-}O{-}OC{-}R_c \end{array}$$

Generalized Triglyceride

where R_a, R_b, and R_c are the same or different and represent the hydrocarbon chain residues of fatty acids. In simple terms, this means that most oils are mixed triglycerides. The triglycerides are produced by the condensation reaction that occurs between a glycerol molecule and three fatty acid molecules:

$$\underset{\text{Glycerol}}{HOCH_2{-}CH(OH){-}CH_2OH} + \underset{\text{Fatty Acid}}{3\,R_xCOOH} \longrightarrow \underset{\text{Triglyceride or Drying Oil}}{R_xCOOCH_2{-}CH(OOCR_x){-}CH_2OOCR_x} + \underset{\text{Water}}{3\,H_2O}$$

where R_x is anyone of R_a, R_b, or R_c. This reaction is reversible and when the oils are heated they can transesterify with R_a, R_b, and R_c capable of changing their positions in an inter- and an intramolecular sense. Drying oils also contain saturated glycerides of fatty acids, but these are usually present at relatively low levels and they do not participate in drying or polymerization phenomenon. Hydrolysis of drying oils results in separation into glycerol and the fatty acid.

Drying oils can be classified in many ways, but one principle way is to divide them into drying, semidrying, and nondrying (an oxymoron term) oils in accordance with their iodine values, which is a measure of unsaturation content. Although such classification has been rather arbitrary, Rheineck and Austin [*2*] defined the classes as given in Table 1.

The main fatty acids found in drying oils and their chemical composition are given in Table 2. The unsaturated-component content of selected drying oils was given in Table 3. Stearic (18-carbon) and palmitic (16-carbon) acids are the most widely distributed saturated fatty acids found in drying oils. Except for cottonseed oil, which contains 29% palmitic acid, the drying oils listed in Table 3 contain less than about 10% of any particular saturated fatty acid residue. The degree of double bond unsaturation controls the drying rate. The higher the degree of unsaturation or iodine number (see below), the faster the drying or polymerization of the oil. Double bond position is also important because conjugated bonds, which is the term used to described two carbon-carbon double bonds separated by one carbon-carbon single bond, are more susceptible to autooxidation [*4*].

Physical characteristics of some typical commercial drying oils are given in Table 4. The oils are particularly characterized by their Iodine Value, which is a measure of the amount of unsaturation present, and Saponification Number, which is an indication of fatty-acid chain molecule weight. Selected property requirement ranges or minimum values for various

TABLE 1—Classification of drying oils by iodine value.

Oil Class	Iodine Value
Drying oil	>140
Semidrying	125–140
Nondrying	<125

[1]Senior Consultant, Consolidated Research, Inc., 1513 Brentwood Road, Charleston, WV 25314-2307.

[2]Information about this industry is developed by the U.S. Department of Commerce. The nature of this market results in information that is usually a few years out of date.

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TABLE 2—Main unsaturated fatty acids found in drying oils.

Fatty Acid	No. Carbon Atoms	No. Double Bonds	Structural Formula
Linolenic	18	3	$HOOC(CH_2)_7CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH_3$
Linoleic	18	2	$HOOC(CH_2)_7CH{=}CHCH_2CH{=}CH(CH_2)_4CH_3$
Oleic	18	1	$HOOC(CH_2)_7CH{=}CH(CH_2)_7CH_3$
Eleostearic	18	3	$HOOC(CH_2)_7CH{=}CHCH{=}CHCH{=}CH(CH_2)_3CH_3$
Licanic	18	3	$HOOC(CH_2)_2CH(O)(CH_2)_4CH{=}CHCH{=}CHCH{=}CH(CH_2)_3CH_3$
Ricinoleic	18	1	$HOOC(CH_2)_7CH{=}CHCH_2CH(OH)(CH_2)_5CH_3$

drying oils and the ASTM method that contains other specification properties are delineated in Table 5. The ASTM methods cited in Table 5 contain references to other ASTM methods appropriate for obtaining the indicated properties and for other pertinent properties. The following drying oils are the most important members of this class of coating raw materials.

Castor oil is obtained from beans of the plant *Ricinus communis*. The oil differs from the other oils in that it is made up of a very high percentage of the hydroxyl-containing ricinoleic acid residue. Although the fatty acid residues in this oil contain on the average only a single double bond and for this reason castor oil is essentially a nondrying oil, it can be converted into a drying oil by a dehydration process in which its hydroxyl group and an adjacent hydrogen atom are removed as water to form a double bond conjugate to the previously existing double bond. The resultant product is known as dehydrated castor oil, which has good drying characteristics.

Cottonseed oil is obtained from the plant *Gossypium malvaceae*. Although it is a drying oil, cottonseed oil is seldom used as an oil in the paint and coating industry. Its main use is as a source of fatty acids that are used in the manufacture of alkyd resins.

Linseed oil, which is obtained from seed of the flax plant *Linum usitatissimum*, is the most common and widely used oil. It has a high degree of unsaturation, which imparts a short drying time, due to its large percentages of linolenic and linoleic triglycerides. It is marketed in a number of modifications including alkali-refined, acid-refined, boiled, blown, and polymerized linseed oil [2]. Polymerized linseed oils of various acid values and viscosities are available.

Oiticica oil is obtained from the nuts of the tree *Licana rigida*. It has a very high licanic acid content, and the three conjugated double bonds of this acid result in rapid drying characteristics. It is often used as an alternative or supplement to tung oil.

Safflower oil is obtained from seed of the plant *Carthamus tinctorius*. This semidrying oil has drying characteristics between those of linseed and soybean oils. Because of its low linolenic acid content, it has low residual unsaturation after cure and very good anti-yellowing characteristics.

Soybean oil is obtained from the seeds of the widely grown plant *Soja hispida*. Its main use is in the preparation of alkyds. It has a wide variety of uses other than as a drying oil. In an epoxidized form, this oil is widely used as a reactive plasticizer and as an acid scavenger. Both epoxidized soybean and linseed oil have been reacted with acrylic acid to form products with residual acrylate functionality and markedly higher viscosity. These acrylated oils have been used as components in radiation-cure coating systems that are initiated with free radicals.

Although tall oil is classified as a drying oil, it is not a triglyceride. The product is obtained as the major byproduct of sulfate or Kraft pulping of pine and certain other softwoods such as spruce and hemlock that are pulped in Scandinavian countries. Crude tall oil is an approximately 50/40/10 by weight mixture of fatty acids, rosin acids, and unsaponifiable compounds such as higher alcohols, waxes and other hydrocarbons, and sterols.

Tung oil is obtained from seeds of the trees *Aleurites fordii* and *Aleurites montana*. This relatively high viscosity and refractive index oil is rapid drying and is used in varnishes and alkyds where water resistance is of principal importance. This oil is also known as wood oil, Chinese wood oil, chinawood oil, and mu oil.

Fish oils are the only nonvegetable oils in the drying oil class. They are principally obtained from menhaden (Alosa menhaden). These oils are semidrying in nature and contain a significant amount of saturated fatty acid residues. In addition to 16 and 18-carbon fatty acid residues, fish oils contain

TABLE 3—Weight percentage of major unsaturated fatty acid residues in selected drying oils [2,3] (remainder of oils is essentially all saturated fatty acid residues).

Drying Oil	Unsaturated Fatty Acid					
	Linolenic	Linoleic	Oleic	Eleostearic	Licanic	Ricinoleic
Cottonseed	...	40	24	...	...	...
Castor	...	3	7	...	...	87
Linseed	52	16	22	...	...	...
Oiticica	...	...	6	...	78	...
Safflower	1	75	13	...	...	...
Soybean	9	51	25	...	...	...
Sunflower[a]	2	75–52	34–14	...	...	...
Tall Oil Fatty Acids	3	41	46	...	...	...
Tung	3	4	8	80	...	...

[a]There is wide variation in reported values for sunflower oil.

TABLE 4—Physical characteristics of some typical drying oils [5].

Oil	Specific Gravity, 25.5/25.5°C	Iodine Value, Wijs	Saponification Value	Acid Value	Refractive Index, 25°C
Cottonseed	0.919	105	192	1.0	1.465
Dehydrated castor	0.931	135	190	5.0	1.481
Fish	0.925	158	187	4.0	1.485
Linseed	0.926	180	190	3.0	1.478
Oiticica	0.967	150	190	4.0	1.510
Safflower	0.922	145	192	2.0	1.474
Soybean	0.920	135	190	2.5	1.473
Sunflower	0.917	135	192	2.0	1.473
Tall oil	...	133	196	194.0	...
Tung	0.915	170	192	0.2	1.517

30 to 40% of arachidonic (20-carbon with four double bonds), clupanodonic (22-carbon with five double bonds), and nisinic (24-carbon with five double bonds) acid residues. Because of the presence of acid residues with high degrees of unsaturation, fish oils have a strong tendency to yellow after cure due to residual unsaturation. Fish oils do represent a source of the very long chain fatty acids that are not present in vegetable oils. Currently, they are not widely used in the coatings' industry with use often dictated by relative price of linseed and soybean oils.

Although raw drying oils are used in coating formulations, the oils are often further processed before use. Such processing includes alkali refining, dehydration, drier addition, heat polymerization that involves heating an oil to selectively advance molecular weight and viscosity, and oxidation or blowing wherein air is bubbled into heated oil and oxygen is taken up with a resultant molecular weight increase. Drying oils are also modified by reaction with maleic anhydride, by copolymerizing with vinyl monomers such as styrene, and by epoxidation.

Reaction with oxygen is the most important reaction that drying oils undergo in the drying or polymerization process [6,7]. Oxidation can result in trans isomer formation, cleavage of the carbon-carbon chain along with formation of volatile byproducts, and polymerization. These reactions can be catalyzed with metallic salts such as cobalt napthenate (see next chapter) that promote free radical formation by reaction with hydroperoxides and other peroxides that are formed in the oxidation process [8]. Farmer and coworkers [9] were first to describe the mechanism of autooxidation wherein they found that four different monohydroperoxides were formed when oxygen was reacted with the methyl ester of oleic acid. A different reaction path was involved when linoleic esters were autooxidized since two monohydroperoxides and one cyclic diperoxide were formed. Polymerization is initiated by reaction of oxygen with an unsaturated fatty acid residue and free radical formation followed by chain propagation in which free radicals react with oxygen to form peroxy radicals which in turn react with other unsaturation sites [10]. The polymerization is terminated by combination of various free radicals that exist in the reaction mass. Availability of multiple double bonds in some of the molecules results in a crosslinked polymeric network.

Solidification or polymerization of a drying oil such as linseed oil can be thought of in the following manner. When the drying oil is exposed to air, there is an induction period during which oxygen is absorbed and it consumes antioxidants present in the system. In this step, there is very little apparent change in physical or chemical properties. This is followed by a period in which there is a marked oxygen uptake and an appearance of peroxides which decompose to form free radicals. The free radicals then initate an addition polymerization of the unsaturation and a crosslinked network results. During the reaction scheme, low molecular weight cleavage products including carbon dioxide and water are formed.

ASTM D 1640 Standard Test Methods for Drying, Curing, or Film Formation of Organic Coatings at Room Temperature has procedures recommended for determination of the stages and rates of film formation in the drying or curing of organic coatings that are to be used at room temperature. Included are methods for determining tack-free, dry-to-touch, dry-hard, dry-through, print-free, and dry-to recoat times. In one instance (Section 7.5.1) a particular procedure is specified for drying oils. ASTM Standard Test Method for Gel Time of Drying Oils (D 1955), deals with determination of the gel time of oiticiica and tung oil. This simple test method, which involves heating the oil in a test tube and observing the time required for the oil to congeal around glass rod relative to a standard of known behavior, can be used for other oils

TABLE 5—Selected property requirements for drying oils (indicated ASTM method has other requirements).

Oil	Specific Gravity, 25/25°C	Iodine Value, Wijs	Saponification Value	Acid Value, max	ASTM Method
Castor, raw	0.957–0.961	83–88	176–184	2.0	D 960
Dehydrated castor	0.926–0.937	125–145	188–195	6	D 961
Linseed, raw	0.926–0.931	177 (min)	189.0–195.0	4.0	D 234
Oiticica	0.972 (min)	135 (min)	None	8.0	D 601
Safflower	0.922–0.927	140–150	189–195	3.0	D 1392
Soybean, refined	0.917–0.924	126 (min)	189–195	0.3	D 1462
Tung, raw	0.933–0.938	163	189–195	5.0	D 12

that have conjugated double bond or other gelling characteristics. ASTM Standard Guide for Testing Drying Oils (D 555) is an overall guide to selection and use of procedures for testing drying oils that are commonly used in coatings.

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5

Driers and Metallic Soaps

by Marvin J. Schnall[1]

METALLIC SOAPS ARE COMPOUNDS of alkaline metals or heavy metals and monobasic carboxylic acids containing from 7 to 22 carbon atoms. The water-insoluble metallic soaps are of particular interest to the coatings industry, although potassium and lithium soaps have limited water solubility.

The applications of metallic soaps in coatings include their use as driers, catalysts, stabilizers, biocides, bodying agents, and flatting agents. An overview of metallic soap applications is presented in Table 1. This chapter concentrates primarily on metallic soaps used as driers, although a brief review of bodying and flatting applications is included.

METALLIC SOAPS AS BODYING AND FLATTING AGENTS

Aluminum stearates, aluminum octoates, and calcium linoleate pulp were at one time widely used as bodying and pigment-suspending agents in solvent-based coatings. Their advantages include fairly high efficiency and ease of incorporation. However, they have a number of deficiencies, including sensitivity to variations in the formulation and in the processing of paints, as well as adverse effects on film hardness and resistance properties. As a result, they have been replaced to a considerable extent by the bentonite clay and organic wax derivatives [*2*].

Zinc and calcium stearates are used on occasion as flatting additives in clear solvent-based coatings. However, precipitated and fumed silicas are now more commonly used for this purpose. Zinc stearate is also used to facilitate sanding of primers and sealers for wood furniture finishing [*2*].

THEORY OF OXIDATIVE DRYING AND FUNCTION OF DRIERS [*1,5*]

It is generally accepted that vehicles based on unsaturated oils, including alkyd resins and oleoresinous varnishes, dry by oxidation according to the following steps:

1. Induction period.
2. Oxygen absorption.
3. Peroxide formation.
4. Peroxide decomposition to free radicals.
5. Free radicals promote cross-linking.

TABLE 1—Coatings applications of metallic soaps.

Applications	Metals	Acids
Driers	Cobalt, manganese, lead, iron, rare earth, cerium, zirconium, zinc, calcium, barium, bismuth, potassium, vanadium, aluminum	Tallates, octoates, naphthenates, neodecanoates, synthetic acids, linoleates, rosinates
Catalysts	Potassium, lithium, cobalt, copper, tin, zinc, manganese	Octoates, naphthenates, laurates, neodecanoates
Stabilizers	Barium, cadmium, tin, zinc, calcium, lead	Proprietary, sulfates, carbonates, stearates
Biocides	Copper, tin, zinc, mercury	Naphthenates, octoates, phenyl acetates, phenyl oleates, laurates, butyl oxides
Bodying agents	Aluminum, calcium	Stearates, octoates, linoleates
Flatting agents	Zinc, calcium	Stearates

The induction period occurs because most drying oils contain natural antioxidants, the effects of which must be overcome before the drying process can begin. Oxygen is then absorbed from the air at the unsaturated sites on the oil molecule, and, as the absorption continues, forms peroxides. These peroxides then decompose to form free radicals which act as catalysts to promote cross-linking of the oil or resin molecules at the unsaturated sites, resulting in dried films.

These steps will occur in the absence of driers, but driers accelerate the process by means of the following mechanisms [*1,5*]:

1. Removal of natural antioxidants.
2. Acceleration of oxygen absorption.
3. Acceleration of peroxide decomposition.

Naturally occurring antioxidants may be considered as negative catalysts for oxidation, whereas driers are positive catalysts, counteracting the effects of the antioxidants.

The multivalent nature of the drier metal is considered to be a key factor accelerating oxygen absorption in the film. The drier metal is initially in a divalent state and is converted to a trivalent state by the presence of oxygen in the film. The metal then releases the oxygen to the film and is converted back to the divalent form. This action accelerates the process

[1]Coatings consultant, 620 Airport Rd., Suite 304, Chapel Hill, NC 27514.

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of oxygen absorption, peroxide formation, and peroxide decomposition, which is responsible for oxidative film drying.

DESCRIPTION OF DRIER METALS

The metals that act as catalysts to promote oxidation and which may be used in driers are indicated below:

Cobalt	Active	Lead	Auxiliary
Manganese		Calcium	
Vanadium		Zirconium	
		Zinc	
		Iron	
		Rare Earth	
		Cerium	
		Aluminum	

Cobalt and manganese, particularly cobalt, are the most active drier metals. Cobalt promotes surface drying of films, while manganese affects both surface and through drying. Vanadium has been mentioned in the literature as an active drier but is seldom used in coating formulations.

The auxiliary driers are seldom used alone, but rather in combination with cobalt and/or manganese. Their functions are to increase the efficiency of the active drier metals and to increase film hardness. In the past, lead was the most frequently employed auxiliary drier, but it is presently out of favor due to toxicity. Calcium and zirconium driers are most frequently used as lead replacements. Zinc is used primarily for improved film hardness and to prevent wrinkling of thick films. Iron driers are used mainly to improve drying of baking systems when their dark color can be tolerated. Rare earth and cerium driers are recommended occasionally for improved through drying and as oxidation catalysts for baking. Interest in aluminum compounds as auxiliary driers has increased recently with the advent of high-solids alkyd resins. Aluminum compounds are being recommended to improve film hardness with these resins but may at times adversely affect viscosity stability and promote gelation.

DESCRIPTION OF DRIER ACIDS

To perform their function, driers should be soluble in the vehicles to which they are added. Solubility is achieved by reacting the drier metals with organic acids to form metallic soaps. The most commonly employed acids are as follows:

- Linoleates
- Rosinates
- Tallates
- Naphthenates
- Octoates (2-ethyl hexanoates)
- Synthetic acids
- Neodecanoates

Chronologically, the linoleates, rosinates, and tallates were the first types developed, followed by the naphthenates and the octoates. A more recent development is the synthetic acid type, which is proprietary but closely related to the octoates. The synthetic acid and neodecanoate driers can be prepared at higher metal concentrations than the other types and are gradually replacing the older acids.

Water-dispersible driers may be prepared by adding nonionic surfactants to naphthenate or synthetic acid driers. However, proprietary cobalt and manganese drier compounds are available that are purported to be more suitable for water-based coatings.

Trade names of the various commercial drier types available are listed in Table 2.

MISCELLANEOUS DRIERS

Restrictions on solvent emissions have stimulated the development of both higher-solids and water-reducible coatings. In the process of formulating these coatings, chemists are experiencing difficulty obtaining satisfactory drying properties with the conventional metallic soap driers. Alternative drier compounds, including both organics and proprietary metallic complexes, are currently being offered [6]. Some typical examples are shown in Table 3. They are usually recommended in combination with conventional metallic soap driers for improved drying efficiency.

Another class of metallic compounds closely related to driers are loss of dry inhibitors or "feeder" driers. These are compounds designed to prevent loss of drying efficiency of paints on aging resulting from the adsorption of driers by pigments, particularly carbon black and organic red pigments. They function by dissolving gradually into the coating vehicle so that the metals are available over a period of time rather than immediately. In this manner, they replace the drier metals that have been adsorbed by the pigments,

TABLE 2—Commercial drier types [3].

Type of Drier	Trade Name	Supplier
Synthetic acid	Cem-All	Mooney Chemical, division of OMG
	NuXtra	Huls America
	Troymax	Troy Corp.
Octoate	Hex-Cem	Mooney Chemical, division of OMG
	Octoate	Huls America
Neodecanoate	Ten-Cem	Mooney Chemical, division of OMG
Naphthenate	Nap-All	Mooney Chemical, division of OMG
	Nuodex	Huls America
	Troykyd	Troy Corp.
Tallates	Lin-All	Mooney Chemical, division of OMG
Water dispersible	Hydro-Cem	Mooney Chemical, division of OMG
	Hydro-Cure	Mooney Chemical, division of OMG
	Nuocure	Huls America
	Troykyd WD	Troy Corp.
	Calcicat	Ultra adhesives
	Aquacat	Ultra adhesives
	Magnacat	Ultra adhesives
	Zircat	Ultra adhesives

TABLE 3—Alternate drier compounds.

Trade Name	Company	Composition
Activ-8	R. T. Vanderbilt Co.	1,10-phenanthroline
Dri-RX	Mooney Chemicals Inc.	2,2′-dipyridyl
Drymax	Huls America	2,2′-dipyridyl
Nutra ADR 10%	Huls America	proprietary metal complex
Nutra LTD 18%	Huls America	proprietary metal complex

thereby maintaining satisfactory drying on prolonged storage. Lead compounds, including litharge, were used formerly but have been replaced by lead-free compounds based primarily on less soluble forms of cobalt and other drier metals.

Commercially available feeder driers are listed in Table 4. All are lead-free metal complexes except for the last item [*3*].

DRIER LEVELS IN COATINGS

Drier requirements for coatings are usually expressed in terms of percent drier metal based on oxidizable vehicle nonvolatile content. A typical calculation is as follows [*1*]:

Assume:

1. In a 1000-g paint formulation, there are 300 g of vehicle nonvolatile.
2. Cobalt drier used is 12% metal by weight.
3. Calcium drier used is 10% metal by weight.
4. Required for optimum drying: 0.05% cobalt plus 0.2% calcium (percent metal based on vehicle nonvolatile).

per 1000 g of paint:

$$\text{Cobalt metal required} = 0.0005 \times 300\text{ g} = 0.15\text{ g}$$
$$\text{Calcium metal required} = 0.002 \times 300\text{ g} = 0.6\text{ g}$$

$$(10\%\text{ calcium drier required}) = \frac{(0.6\text{ g calcium metal})}{(0.10\text{ g metal/g drier})} = (6\text{ g drier as supplied})$$

$$(12\%\text{ cobalt drier required}) = \frac{(0.15\text{ g cobalt metal})}{(0.12\text{ g metal/g drier})} = (1.25\text{ g drier as supplied})$$

The optimum levels of drier metal required will vary depending on the type of resin system employed and the conditions of drying. Typical metal concentrations for a number of common vehicles are indicated in Table 5.

TABLE 4—Commercial feeder driers.

Company	Trade Name
Mooney Chemical, division of OMG	Hex-Cem LFD
Mooney Chemical, division of OMG	Hydroxy Ten-Cem Cobalt
Troy Corporation	Troykyd Perma Dry
Huls America	Nuact Cobalt 254
Huls America	Nuact NOPB
Huls America	Nuact Paste (lead-based)

TESTING OF DRYING EFFICIENCY

The procedures used to determine the stages of film formation during the drying of coatings are described in ASTM Test Methods for Drying, Curing, or Film Formation of Organic Coatings at Room Temperature (D 1640) [*4*]. With coatings containing metallic driers, it is recommended that the paint samples age overnight following the drier additions before drying tests. The drying conditions, shown in Table 6, are usually specified but are subject to agreement between the purchaser and the seller.

The methods used to determine the various stages of drying may be summarized as follows:

1. *Set-To-Touch-Time*—no transfer of the coating upon lightly touching the film with the finger.
2. *Dust-Free-Time*—(a) cotton fibers dropped on the film can be removed by blowing lightly; (b) fine calcium carbonate extender dropped on the film can be completely removed by blowing gently and wiping with a cloth or brush.
3. *Tack-Free-Times*—a specified type of paper or aluminum foil will no longer adhere to the film when applied under specific conditions.
4. *Dry-To-Touch-Time*—the film no longer adheres to the finger when pressed firmly and does not rub up when rubbed lightly.
5. *Dry-Hard-Time*—a thumb print applied under specified conditions is completely removed from the film when polished lightly with a soft cloth.
6. *Dry-Through-Time*—the film is not distorted or detached when the thumb is applied to it in a specified manner and rotated through a 90° angle.
7. *Dry-To-Recoat*—a second coat or top coat can be applied without development of lifting or loss of adhesion of the first coat.
8. *Print-Free-Time*—army duck or cheesecloth applied at a pressure of 3.5 or 6.9 KPa no longer marks the film as determined by photographic standards shown in ASTM Test Method for Print Resistance of Lacquers (D 2091) [*4*].

In addition to the above subjective tests, a number of mechanical drying time recorders are available. The instrument referred to most frequently in recent literature is the Byk-Gardner Improved Circular Drying Time Recorder [*7*]. This functions by moving a Teflon stylus over the applied film in a circular path. The pattern left in the film by the stylus after a complete revolution is observed. Recorders are available which make complete revolutions in 1, 6, 12, or 24-h. With the use of a plastic template, set-to-touch, surface dry, and through-dry times may be noted.

Development of film hardness is also an important criterion of drier efficiency. Tests [*4*] used to measure hardness include:

1. *Test Method for Film Hardness by Pencil Test (D 3363)*—a series of pencils varying in lead hardness from 6B (softest) through 6H (hardest) are pushed into the film, and the hardest pencil that will not penetrate the film is noted.
2. *Test Method for Hardness of Organic Coatings by Pendulum Damping Tests (D 4366-87)*—either a Konig or a Persoz Pendulum Hardness Tester is employed with the time, in seconds, noted for the swing amplitude of the pendulum to

TABLE 5—Typical drier recommendations, percent metal based on vehicle nonvolatile.

	Cobalt	Manganese	Zirconium	Calcium	Zinc	1,10-Phenanthroline	2,2'-Dipyridyl, 30%
Long oil alkyd-air dry	0.04–0.06			0.1–0.3			
	0.04–0.06			0.1–0.3			
	0.04–0.06		0.1–0.2	0.1–0.2			
Medium oil alkyd-air dry	0.04–0.06		0.1–0.3				
	0.04–0.06			0.1–0.3			
	0.04–0.06		0.1–0.2	0.1–0.2			
Short oil alkyd air-dry	0.04–0.06		0.1–0.3				
	0.04–0.06			0.1–0.3			
	0.04–0.06		0.1–0.2	0.1–0.2			
Chain-stopped alkyd	0.05–0.08			0.2			
	0.05–0.08		0.1	0.1			
Medium oil alkyd-bake	0.01–0.03				0.1–0.5		
Oil-modified urethane	0.02–0.04		0.1–0.3				
	0.02–0.04			0.1–0.3			
		0.02–0.04				0.2	
Linseed oil	0.02	0.02	0.1–0.2	0.1–0.2			
		0.02–0.04	0.1–0.3		0.1–0.15		
		0.02–0.04		0.1–0.3			
Alkyd-oil house paint	0.02–0.03	0.02–0.03		0.2–0.3			
	0.02–0.03	0.02–0.03	0.2–0.3				
	0.02–0.04	0.02–0.04	0.1–0.2	0.1–0.2	0.1–0.15		
Epoxy Ester	0.03–0.05		0.1–0.2				
	0.03–0.05			0.1–0.2			
Acrylic Modified alkyd	0.04–0.08		0.1	0.1			
Oleoresinous varnish	0.02–0.06			0.2			
Vinyltoluene alkyd	0.02–0.04		0.1				
	0.02–0.04			0.1			
High solids alkyd	0.04–0.06		0.5–0.9			0.2	
		0.04–0.06		0.5–0.9		0.2	
	0.04–0.06		0.2–0.4				0.2–0.4
Water-based alkyds (water dispersible driers)	0.04–0.06		0.1–0.3				
	0.04–0.06			0.1–0.3			
	0.05–0.1		0.15–0.3	0.15–0.2			0.1–0.3

decrease by a specified degree when set into oscillation on the dried film.

3. *Test Methods for Indentation Hardness of Organic Coatings (D 1474)*—either a Knoop or a Pfund Indenter is applied to a film under a specified loading, and the depth of indentation is measured with the aid of a microscope. The depth is converted to either a Knoop or a Pfund Hardness Number using the equations in the standard.

TABLE 6—Standard drying conditions.

Condition	Typical Value
Ambient temperature	23 + 2°C
Relative humidity	50 + 5%
Film thickness (dry)	12.5 to 45 μm
Substrate	Clean glass
Lighting	No direct sunlight
Applicators	Doctor blades
Coating viscosity	Close to normal application

SPECIFICATIONS FOR LIQUID PAINT DRIER

Drier specifications as described in ASTM Specification for Liquid Paint Driers (D 600) involve the following classes:

Class A	2-ethyl hexanoic acids in petroleum spirits.
Class B	Naphthenic acids in petroleum spirits.
Class C	Neodecanoic acids in petroleum spirits.
Class D	Tall oil fatty acids in petroleum spirits.
Class E	Any of the above, plus additives to make the driers water dispersible.
Class F	Other unidentified acids and acid blends.

A comprehensive table of liquid paint driers of the above classes is given in ASTM D 600 [*4*]. The typical properties of the driers listed and reproduced in Table 7 include percent metal concentration, percent nonvolatile content, specific gravity, Gardner Color, and Gardner-Holdt viscosity.

TABLE 7—Typical requirements of liquid paint driers.[a]

Class	Metal	Metal Concentration, % Min	Metal Concentration, % Max	Nonvolative Matter, %, Max	Typical Specific Gravity, 25/25°C Min	Typical Specific Gravity, 25/25°C Max	Color[b] Gardner (Test Method D 1544)	G-H Viscosity (Test Method D 1545)
A	Calcium	3.9	4.1	50	0.884[c]	...	3	A
A	Calcium	4.9	5.1	60	0.894	0.912	5	C
B	Calcium	3.9	4.1	70	0.902	0.937	10	D
B	Calcium	4.9	5.1	85	0.932	0.970	11	T
C	Calcium	4.9	5.1	46	0.888	...	2	A
D	Calcium	3.9	4.1	66	0.890	0.918	9	B
E	Calcium	3.9	4.1	63	0.905	0.930	8	G
E	Calcium	5.9	6.1	76	0.922	0.960	5	N
F	Calcium	3.9	4.1	50	0.850	0.884	3	A
F	Calcium	4.9	4.1	60	0.900	0.936	4	B
F	Calcium	5.9	6.1	74	0.873	0.948	6	N
F	Calcium	7.9	8.1	70	0.958	...	5	B
F	Calcium	9.9	10.1	65	1.000	1.030	7–8	K
A	Cerium	5.9	6.1	30	0.856	...	8	A
B	Cerium	5.9	6.1	57	0.925	...	17	A1
A	Cobalt	5.9	6.1	45	0.875	0.900	Blue/purple	A
A	Cobalt	11.8	12.2	90	1.008	1.060	Blue/purple	J
B	Cobalt	5.9	6.1	67	0.918	0.970	Blue/purple	B
C	Cobalt	11.8	12.2	65	0.984	...	Blue	A
D	Cobalt	5.9	6.1	72	0.912	0.956	Purple	C
E	Cobalt	4.9	5.1	60	0.926	...	Red/purple	A
E	Cobalt	5.9	6.1	71	0.945	0.960	Blue/purple	I
F	Cobalt	5.9	6.1	70	0.870	0.958	Blue/violet	A
F	Cobalt	11.8	12.2	80	1.014	1.040	Blue/violet	J
A	Iron	5.9	6.1	50	0.900	0.930	Dark brown	A
B	Iron	5.9	6.1	67	0.960	0.990	Dark brown	M
F	Iron	5.9	6.1	50	0.905	0.930	Brown	A
F	Iron	8.9	9.1	78	0.950	0.985	Brown	A
F	Iron	11.8	12.2	75	1.068	...	Brown	A
A	Lead	23.8	24.2	65	1.090	1.110	3	A
B	Lead	23.8	24.2	67	1.125	1.160	11	B
C	Lead	23.8	24.2	61	1.100	...	2	B
D	Lead	23.8	24.2	66	1.100	1.125	10	A2
E	Lead	23.8	24.2	71	1.125	1.150	7	A
F	Lead	23.8	24.2	67	1.080	1.140	10	A
F	Lead	35.8	36.2	81	1.350	1.393	8	H
A	Manganese	5.9	6.1	50	0.888	0.920	Red/brown	A
B	Manganese	5.9	6.1	66	0.930	0.965	17	D

Continued

TESTING OF LIQUID PAINT DRIERS

ASTM Test Method for Liquid Paint Driers (D 564) [*4*] outlines the test procedures employed, including both physical and chemical tests. The physical tests include:

1. *Appearance*—observations for clarity and cleanness in accordance with ASTM Test Method for Clarity and Cleanness of Paint Liquids (D 2090).
2. *Color*—according to ASTM D 1544, which employs the Gardner numerical color scale. However, a number of driers, including cobalt, manganese, nickel, and rare earth, do not fit into this scale and are reported descriptively.
3. *Nonvolatile Content*—According to ASTM D 1644, Method A or B. Method A involves heating samples at 105°C for 10 min, while Method B specifies 150°C for 10 min.
4. *Miscibility with Oil*—One volume of the drier sample is mixed with 19 volumes of raw linseed oil. The mixture is observed for any signs of separation or clouding over a 24-h period.
5. *Stability*—The drier sample is stored for 7 days at 25°C, −20°C, and 50°C and examined for indications of clotting, gelation, or precipitation.
6. *Drying power*—As described in the section entitled "Testing of Drying Efficiency."
7. *Viscosity*—According to ASTM Test Method for Viscosity of Transparent Liquid by Bubble Time Method (D 1545). This involves comparing the time of travel of bubbles in tubes of the sample versus Gardner-Holdt standard tubes. The standards were formerly designated by letter but are now indicated directly in stokes. A table in D 1545 indicates the conversion from letters to stokes.

Chemical analysis is used to determine the metal content of liquid paint driers. The EDTA method is used for most drier metals (Table 8). The liquid drier is dissolved or digested in solvents and then treated with an excess of standard EDTA solution (disodium salt of ethylenediamine tetracetic acid dihydrate). The excess of EDTA is then titrated to an end point determined by a specified indicator. This method is applicable to single metal driers only, not to drier blends. An EDTA method is not yet available for cerium, and an oxidimetric determination is specified [ASTM Test Method for Cerium in Paint Driers by Oxidimetric Determination (D 3970)]. Table 8 outlines the ASTM designations, indicators, and titrating solutions for analysis of drier metals by EDTA titration.

TABLE 7—*Continued*

Class	Metal	Metal Concentration, % Min	Metal Concentration, % Max	Nonvolative Matter, %, Max	Typical Specific Gravity, 25/25°C Min	Typical Specific Gravity, 25/25°C Max	Color[b] Gardner (Test Method D 1544)	G-H Viscosity (Test Method D 1545)
C	Manganese	5.9	6.1	50	0.870	...	10	A
D	Manganese	5.9	6.1	72	0.942	0.972	Brown	E
E	Manganese	4.9	5.1	42	0.911	...	Brown	E
E	Manganese	5.9	6.1	69	0.942	0.965	Brown	E
F	Manganese	5.9	6.1	55	0.870	1.020	18	A
F	Manganese	8.9	9.1	80	0.950	1.020	18	H
F	Manganese	11.8	12.2	75	1.044	...	16	C
A	Nickel	9.9	10.1	70	1.032	...	Green	A
A	Rare earth[d]	5.9	6.1	30	0.630	0.880	6	E
A	Rare earth	11.8	12.2	55	0.977	...	Yellow/green	C
B	Rare earth	3.9	4.1	35	0.840	0.855	10	A
C	Rare earth	5.9	6.1	35	0.876	...	8	A5
A	Zinc	7.9	8.1	50	0.880	0.906	6	G
A	Zinc	17.8	18.2	90	1.068	1.130	7	Z
B	Zinc	7.9	8.1	70	0.915	0.960	9	A
B	Zinc	9.9	10.1	75	0.980	1.044	8	L
D	Zinc	7.9	8.1	70	1.008	...	11	D
E	Zinc	7.9	8.1	42	0.946	...	2	A
F	Zinc	7.9	8.1	60	0.855	0.963	7	C
F	Zinc	15.8	16.2	80	1.020	1.100	3	B
A	Zirconium	5.9	6.1	30	0.860	0.864	2	A
A	Zirconium	11.8	12.2	56	0.960	0.992	4	A
A	Zirconium	17.8	18.2	55	1.070	1.074	3	A
A	Zirconium	23.8	24.2	77	1.240	...	2	J
C	Zirconium	5.9	6.1	23	0.864	...	2	A5
C	Zirconium	11.8	12.2	46	0.976	...	2	A
E	Zirconium	5.9	6.1	31	0.864	...	4	A
E	Zirconium	11.8	12.2	55	0.975	1.020	4	A
F	Zirconium	5.9	6.1	28	0.855	0.870	2	A5
F	Zirconium	11.8	12.2	55	...	...	...	...
F	Zirconium	17.8	18.2	80	1.090	1.130	4	Z
F	Zirconium	23.8	24.2	93	1.240	1.260	6	J

[a]Source: National Paint and Coatings Association, Chemical Specialties Section, Raw Material Index, April 1978 edition per Gardner Method D 1544.
[b]If off the scale, as observed by the unaided eye.
[c]Only one drier was listed in this category.
[d]The metal content represents total rare earth metals calculated as cerium, but the drier contains cerium and lanthanum, as well as minor amounts of other rare earth metals.

TABLE 8—Metal analysis by EDTA titration.

Metal	ASTM Method	Solvent	Indicator	Titrating Solution
Cobalt	D 2373	Glacial acetic acid	PAN[a]	Cupric sulfate
Lead	D 2374	Glacial acetic acid	PAN[a]	Cupric sulfate
Manganese	D 2375	Toluene-ethanol	Eriochrome black-T	Zinc chloride
Calcium or zinc	D 2613	Toluene-ethanol	Eriochrome black-T	Zinc chloride
Iron	D 3804	Isopropanol	Eriochrome black-T	Zinc chloride
Zirc	D 3969	HSO-HO	Xylenol orange	Bismuth nitrate
Vanadium	D 3988	Isopropanol-HCL	Xylenol orange	Zinc chloride
Total rare earth	D 3989	Isopropanol-HCL	Xylenol orange	Zinc chloride

[a]1(2-Pyridylazo)-2-Naphthenol.

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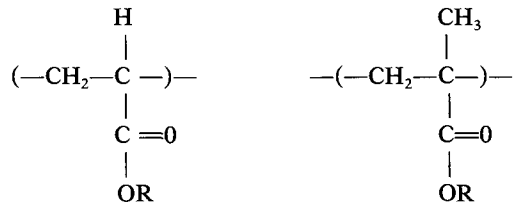
Part 3: Synthetic Materials

6

Acrylic Polymers as Coatings Binders

by John M. Friel[1]

ACRYLIC POLYMERS, WHICH ARE USED as coatings binders, are comprised chiefly of esters of acrylic and methacrylic acid that are polymerized by additional polymerization, usually using a free radical mechanism:



An acrylate A methacrylate

Interest in acrylic technology dates back to the 1920s when Dr. Otto Rohm developed a practical process for making acrylate esters from ethylene. Shortly afterwards, his associate, Otto Haas, established the first commercial production of methyl and ethyl acrylate in the United States [*1*]. The first commercial use of an acrylic polymer was as an adhesive-like interlayer for laminated safety glass. Probably the highest profile use of an acrylic began in 1936 with the introduction of thermoplastic, transparent methacrylate sheet. With the advent of World War II, methacrylate sheet became invaluable as a tough, weather-resistant glazing material for military aircraft. Since it could be formed easily and had excellent optical properties, the transparent plastic was used for aircraft canopies, bomber noses, and gun turrets [*2*].

Acrylic technology soon expanded into the coatings industry in the form of acrylic solution polymers, followed later by acrylic emulsions. The acrylics gained widespread market acceptance as coatings binders due to such outstanding properties as color stability, transparency, and resistance to weathering and aging. The good weathering resistance of acrylic polymers is primarily due to their resistance to hydrolysis and their lack of absorption of ultraviolet (UV) light, the high-energy portion of the light spectrum most responsible for degradation.

Acrylic solution polymers (often referred to as acrylic resins) are generally copolymers of acrylate and methacrylate esters prepared by direct solution polymerization in a solvent that has a solubility parameter similar to that of the polymer. Typical solvents include aromatics such as toluene and xylene, as well as ketones and esters. Acrylic resins are typically supplied at about 30 to 50% solids by weight, with viscosities ranging from a few hundred to a few thousand centipoise. In later years, 100% solid-grade versions became popular since they reduced the cost and safety concerns associated with shipping resins containing high solvent levels. The coatings manufacturer is then able to dissolve the solid-grade acrylic in a wide range of solvents, thereby having greater control over the formulation ingredients.

A wide range of properties can be built into an acrylic coatings binder by careful selection of the type and level of the acrylic monomers used. Some of the important properties for several acrylic homopolymers are shown in Table 1 [*3*]. Coatings for a wide range of applications can therefore be custom designed. Some of the principal applications for acrylic solution coatings include automotive finishing, factory, and farm implement coatings, general-purpose pigmented coatings, aerosol lacquers, and clear coatings for a multitude of substrates. There are two types of acrylic solution polymers: (1) thermoplastic polymers, which harden simply by loss of solvent through evaporation; and (2) thermosetting polymers, which contain functional groups that react with another functional material (i.e., melamine, epoxy, isocyanate, etc.) to form a cross-linked network. The advantages and disadvantages of each are discussed in detail later in this chapter.

Acrylic emulsion polymers (often referred to as acrylic latexes) have become one of the major binder types in use in the coatings industry today. To form an emulsion polymer, the acrylic monomers are emulsified and then polymerized as small droplets in a continuous water phase. The droplets are typically stabilized by surfactants, and usually no solvent is present. While acrylic emulsions are generally associated with quality architectural coatings, they are also used to formulate industrial coatings. In fact, the use of acrylic emulsions in industrial applications is expanding at the expense of

TABLE 1—Properties of polymethacrylates and polyacrylates [*3*].

Polymer Types	Tensile Strength, psi	Elongation, %
Polymethacrylate		
Methyl	9000	4
Ethyl	5000	7
Butyl	1000	230
Polyacrylates		
Methyl	1000	750
Ethyl	33	1800
Butyl	3	2000

NOTE: Psi ÷ 14.22 = kg/cm^2.
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[1]Group leader and research fellow, Architectural Coatings Research, Rohm and Haas Co., Research Laboratories, 727 Norristown Road, Spring House, PA 19477.

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solvent-based systems because of the industry's need to control organic emissions. Over the past 20 years, acrylic emulsion manufacturers have made great strides in improving the properties of acrylic emulsions so that they now offer performance similar to the solvent-based coatings they are replacing.

When the first acrylic emulsion designed for use in house paints was introduced in 1953, it had the low-odor, quick-drying, and easy cleanup features of its water-based competitors, styrene-butadiene and poly(vinyl acetate) emulsions; but, in addition, it offered excellent exterior durability that allowed use in exterior paints. During the past 40 years, it has been good exterior durability that enabled acrylic emulsions to replace solvent alkyds as the dominant binder in the exterior house paint market.

ACRYLIC SOLUTION POLYMERS

Thermoplastic Resins

Thermoplastic acrylic resins are acrylic polymers that are polymerized directly in a suitable solvent and form a film solely by evaporation of the solvent. They do not need to be oxidized or cross-linked to form a hard, resistant finish. They are fast-drying lacquer materials, but they remain permanently soluble.

Acrylic resins are usually supplied in strong solvents such as toluene, xylene, or methyl ethyl ketone. They are clear, colorless solutions and, if left unpigmented, will also dry down to clear, colorless films. They are often used in unpigmented form as protective finishes over vacuum metalized plastics and polished metals such as brass.

Acrylic resins generally make excellent grind media for dispersing pigments. No external pigment wetting agents are required to make finely dispersed pigment grinds for high-gloss lacquers. Also, thermoplastic acrylic polymers are quite unreactive and consequently are stable when mixed with pigments, extenders, and colors. They do not discolor powdered metals, such as aluminum.

Acrylics are a uniquely versatile family of polymers since an infinite array of properties can be achieved by carefully selecting combinations of the various acrylic monomers. Each acrylic monomer brings to the polymer its own individual performance characteristics based on its molecular structure. This is particularly true for polymer hardness as determined by the glass transition temperature (T_g) of the monomers that make up the homopolymer (only one monomer) or copolymer (two or more monomers). The T_g of a polymer is a softening point: it is actually a temperature range where the polymer undergoes a second-order transition. At temperatures below the T_g, the polymer is a glass, but above the T_g the polymer is a rubbery material. To approximate the T_g for a copolymer composition, it is useful to utilize the relationship proposed by Fox [4].

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{1}$$

where

W_1 and W_2 = the weight ratios of Monomers 1 and 2, respectively,

T_{g1} and T_{g2} = the T_g's of the homopolymers of Monomers 1 and 2 in degrees absolute.

Since thermoplastic acrylics are not cross-linked to achieve a desired level of performance, the concept of T_g and the ability to manipulate T_g as a means to control properties is crucial in designing polymers that meet the needs of the coatings market. The marked difference in T_g's, and consequently polymer characteristics of the acrylics, can phenomenologically be explained by the free-volume theory proposed by Fox and Flory [5] and later refined by several others. The free-volume theory states that the T_g for any given polymer occurs at that temperature where the fractional free volume (i.e., unoccupied space contained within the polymer) reaches some universally constant value that remains unchanged as temperature decreases below T_g. Above this temperature, the free volume increases, permitting sufficient molecular motion so polymer flow can begin. In Fig. 1, Rogers and Mandelkern have plotted specific volume versus temperature for a series of methacrylates as a means of establishing the relationship of T_g to free volume [6]. The arrows (↑) in Fig. 1 indicate the temperature at which there is an inflection in the specific volume curve indicating a sudden increase in free volume (as temperature increases). This is the T_g. From the graph, it can be calculated that, at T_g, free volume accounts for 15% of the total polymer volume [6]. Simha and Boyer have independently calculated that at T_g, free volume accounts for 11% of a polymer's total volume [7].

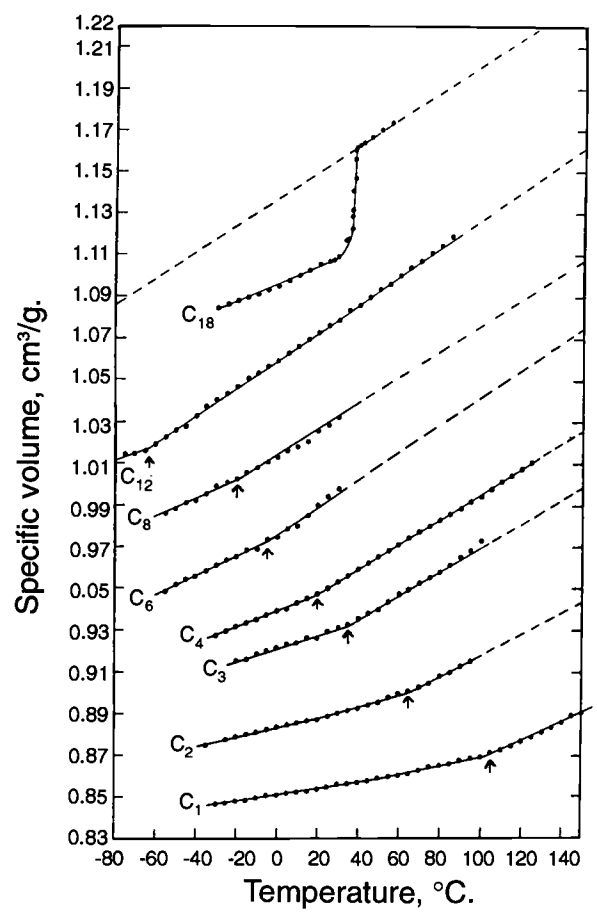

FIG. 1—Specific volume-temperature relations for the poly-(*n*-alkyl methacrylates). (Reprinted with permission from the American Chemical Society. Copyright 1957.)

On a molecular level, the T_g differences for the acrylic family of polymers can also be easily explained. The acrylates have an alpha-hydrogen atom next to the carbonyl group, giving them more rotational freedom and hence greater segmental chain motion than the methacrylates. The methacrylates have a bulky methyl group substituted for the alpha-hydrogen atom, which hinders molecular rotation, thereby increasing chain stiffness. The methacrylates are therefore higher in T_g, harder, higher in tensile strength, and lower in elongation than analogous acrylate polymers.

Equally important to T_g and polymer hardness is the length of the ester side chain of the monomer. As the alcohol moiety of the ester side chain becomes larger, the polymer chains are pushed further apart, creating additional free volume, thereby encouraging greater molecular rotation. Consequently, the polymers become increasingly soft (as the ester side chain becomes larger) until the effects of side-chain crystallization causes additional hardening effects. Table 2 demonstrates the large range of T_g's that exist for the acrylate and methacrylate family of homopolymers [8].

The second most important parameter governing the film properties of a thermoplastic acrylic polymer is molecular weight (MW). Most dry film properties for thermoplastic acrylics improve with increasing molecular weight up to a MW of about 100 000 and then tend to level off. Tensile strength, elongation, toughness, solvent resistance, and exterior durability are all dependent on molecular weight. This dependence of strength, elongation, and resistance of the acrylic polymer on molecular weight is primarily due to the greater number of chain entanglements (which act almost like cross-links), anchoring the polymer chains at higher molecular weight (i.e., longer chain length).

However, the viscosity of a solution polymer is proportional to the molecular weight of a polymer according to the Mark-Houwink equation [9].

$$\eta = K(\mathrm{MW})^a \qquad (2)$$

where

η = solution viscosity

K and a = constants derived experimentally for a specific polymer/solvent combination (for polymethyl methacrylate in toluene, $K \times 10^5 = 7.1$ and $a = 0.73$). The type molecular weight used in determining the constants should be specified.

As molecular weight increases, the solution viscosity also increases, thereby posing handling and application problems if the molecular weight becomes too high. For example, high spray solids are desirable for acrylic lacquers because of economy and emissions concerns. The lower the molecular weight of the polymer, the lower the viscosity at a given solids content, or conversely, the higher the spray solids at spray viscosity. Consequently, low molecular weight is beneficial to solids and application concerns, whereas high molecular weight is needed for good film properties.

The obvious answer to the viscosity versus film property dilemma is to reach an optimum balance by producing an intermediate molecular weight polymer. For this reason, most thermoplastic acrylic solution polymers have weight-average molecular weights in the 75 000 to 100 000 range. It is also helpful to narrow the molecular weight distribution, reducing the amount of low-molecular-weight fractions, which have a deleterious effect on resistance and strength properties, while also minimizing high-molecular-weight portions, which increase viscosity and cause application problems such as cobwebbing of spray-applied acrylic automotive lacquers.

Since the application and drying properties of an acrylic resin are largely controlled by the physical characteristics of the solvent contained in the resin, as well as by the interaction of the polymer and solvent, it is essential to carefully select

TABLE 2—T_g for methacrylate and acrylate homopolymers [8].

Polymer	T_g, °C	Polymer	T_g, °C
poly(methyl methacrylate)	105	poly(methyl acrylate)	6
poly(ethyl methacrylate)	65	poly(ethyl acrylate)	−24
poly(*n*-propyl methacrylate)	35	poly(propyl acrylate)	−45
poly(isopropyl methacrylate)	81	poly(isopropyl acrylate)	−3
poly(*n*-butyl methacrylate)	20	poly(*n*-butyl acrylate)	−55
poly(*sec*-butyl methacrylate)	60	poly(*sec*-butyl acrylate)	−20
poly(isobutyl methacrylate)	53	poly(isobutyl acrylate)	−43
poly(t-butyl methacrylate)	107	poly(t-butyl acrylate)	43
poly(*n*-hexyl methacrylate)	−5	poly(hexyl acrylate)	
poly(2-ethylbutyl methacrylate)	11	(brittle pt)	−57
poly(*n*-octyl methacrylate)	−20	poly(heptyl acrylate)	−60
poly(2-ethylhexyl methacrylate)	−10	poly(2-heptyl acrylate)	−38
poly(*n*-decyl methacrylate)	−60	poly(2-ethylhexyl acrylate)	−50
poly(lauryl methacrylate)	−65	poly(2-ethylbutyl acrylate)	−50
poly(tetradecyl methacrylate)	−72	poly(dodecyl acrylate)	
poly(hexadecyl methacrylate)		(brittle pt)	−30
poly(octadecyl methacrylate)	−100	poly(hexadecyl acrylate)	35
poly(stearyl methacrylate)		poly(2-ethoxyethyl acrylate)	−50
poly(cyclohexyl methacrylate)	104	poly(isobornyl acrylate)	94
poly(isobornyl methacrylate)	170(110)	poly(cyclohexyl acrylate)	16
poly(phenyl methacrylate)	110		
poly(benzyl methacrylate)	54		
poly(ethylthioethyl methacrylate)	−20		
poly(3,3,5-trimethylcyclohexyl-methacrylate)	79		

NOTE: The brittle point measured by a fracture test often approximates T_g.

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the solvent in which the acrylic is dissolved (see Chapter 18 entitled "Solvents"). To ensure good solubility of the polymer, it is important to match the solubility parameter of the solvent to that of the polymer. The solubility parameter is an estimation of the polarity of a solvent or polymer and is related to the intermolecular energy of the molecule (see Chapter 35 entitled "Solubility Parameters"). The solubility parameter concept was defined by Hildebrand [*10*] and applied to coatings by Burrell. Burrell has published the solubility parameters for an extensive list of solvents [*11*].

For polymers, the solubility parameter can be calculated by knowing the molecular structure of the repeating unit according to Small's method. Small has published a table of molar attraction constants used to calculate polymer solubility parameters [*12*].

Besides being helpful in estimating solubility, the solubility parameter concept is helpful in predicting the resistance of polymers to solvents or other organics. In general, the more polar acrylic polymers will have the best resistance to hydrophobic materials, such as gasoline, grease, or oil. More hydrophobic acrylics (with low δ values) will have better resistance to polar materials, such as water and alcohol.

The evaporation rate of the solvent or solvent mixture must also be carefully chosen to accommodate the expected application method and conditions. For spray application, moderately fast evaporating solvents are needed to avoid running and sagging of the low-viscosity paint. For roller coating, a much higher viscosity coating would be used; therefore, slower evaporating solvents are required to avoid skinning on the roller and to allow for flowout of roller pattern created during application of the paint. Since thermoplastic acrylics dry by evaporation of solvent alone, extremely slow-drying solvents, which retard development of properties, should be avoided.

The majority of thermoplastic acrylic solution polymers are designed for general-purpose industrial finishing (i.e., metal furniture and product finishing) and have a T_g of approximately 50°C. This T_g is generally obtained by copolymerizing combinations of methyl methacrylate (MMA), butyl methacrylate (BMA), ethyl acrylate (EA), butyl acrylate (BA), and ethylhexyl acrylate (EHA). While many other acrylate and methacrylate monomers exist, as indicated in Table 2, these few are the primary acrylic monomers that are commercially available and that are, therefore, the most economically feasible.

At a T_g of 50°C, these acrylic polymers are intermediate in hardness, having a Tukon hardness of about 11 to 12 [see ASTM Test Methods for Indentation Hardness of Organic Coatings (D 1474)]. They are hard enough to dry rapidly to a tack-free state that allows early handling of the coated product and also hard enough to resist marring, print [see ASTM Test Method for Print Resistance of Lacquers (D 2091)], block [see ASTM Test Method for Blocking Resistance of Architectural Paints (D 4946)], and dirt pickup. Yet, they retain enough flexibility and elongation to have some impact resistance [see ASTM Test Method for Resistance of Organic Coatings to the Effects of Rapid Deformation (Impact) (D 2794)], and some can even be post-fabricated, such as is done with coil coated stock to produce aluminum gutters, trim pieces, etc.

Up to the mid-1950s, nitrocellulose lacquers were the major automotive coating in use. Nitrocellulose finishes gave an excellent original appearance but had poor durability, particularly gloss retention, and required frequent polishing by the car owner for the finish to look good. This problem was eliminated in 1956 when General Motors adopted acrylic lacquers based on poly(methyl methacrylate). The acrylic lacquers gave significantly better durability and allowed for the use of the more modern eye-catching metallic pigments [*13*]. The acrylic lacquers generally contain external plasticizers, such as the phthalates, which contribute to improved chip resistance and cold crack resistance. No internal plasticizing monomer (i.e., acrylates) is generally contained in automotive acrylic lacquers, and consequently their T_g is approximately 105°C, with a Tukon hardness of about 22.

Since they are very hard and fairly high molecular weight (i.e., 100 000), the thermoplastic solution polymers designed for automotive use are not capable of the excellent molecular flow that would be expected of softer/lower-molecular-weight polymers. Consequently, the acrylic lacquers require factory buffing and or baking to obtain the kind of maximum gloss required for the new car showroom. This disadvantage was shared by the older nitrocellulose lacquers.

Also, because of hardness and high molecular weight, the spray solids percent is low. Since these lacquers are thermoplastic, they are permanently subject to softening by strong solvents, such as toluene or acetone, if for some reason they would contact the automotive finish. Conversely, however, the thermoplastic acrylic lacquers can be easily repaired by an additional coat of paint which "melts" into the original coat, leaving no "two-coat" effects or intercoat adhesion problems.

Thermosetting Acrylic Resins

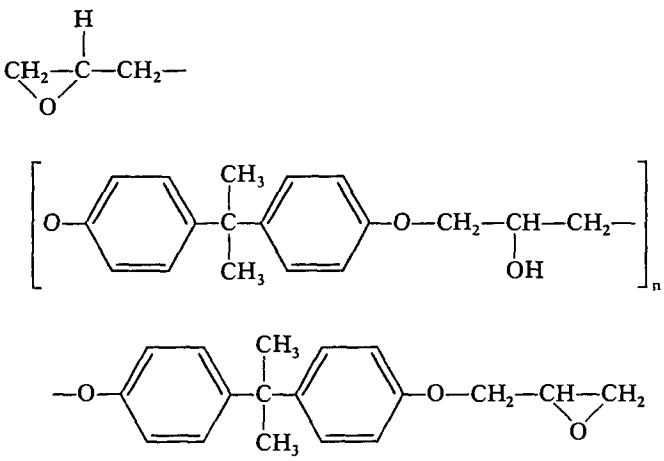
Thermosetting acrylic resins are compositionally very similar to the thermoplastic-type acrylics, with the exception that they contain functional groups, such as carboxyl or hydroxyl, that are capable of reacting with another polymeric or monomeric multifunctional material to produce a three-dimensional network structure. As has already been discussed, the mechanical properties of thermoplastic acrylic polymers for coatings are generally improved by increasing molecular weight, but polymers with overly high molecular weight produce solutions of unworkably high viscosity. An alternate route to improved film properties is to use a thermosetting acrylic polymer, converting linear, moderate-molecular-weight polymer chains to an infinite molecular weight structure. This cross-linking reaction takes place after the coating has been applied to the substrate, often by the application of heat, hence the term "thermosetting." To be truly cross-linked, one of the reactive species must have at least two reactive sites, while the other species has at least three reactive sites per molecule or chain.

Thermosetting acrylic polymers offer the following advantages over thermoplastic acrylics: (1) improved hardness and toughness, (2) better resistance to softening at elevated temperatures, (3) improved resistance to solvents, stains, and detergents, and (4) lower applied molecular weight, resulting in lower solution viscosity and consequently higher application solids.

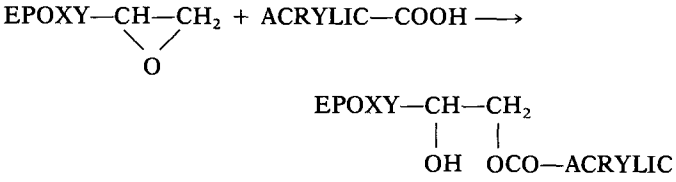
Over the years, numerous chemical reactions utilizing various functional groups have been devised as a means to cross-link acrylic polymers. However, we will elaborate on some of the more commercially significant thermosetting acrylics, namely those cross-linked with nitrogen resins, epoxies, and isocyanates.

Acid-Functional Acrylics Cross-Linked with Epoxy Resins

Possibly the most resistant acrylic enamels are based on thermosetting acrylic solution polymers that contain acid functionality and are reacted with an epoxy resin. Typically, the epoxy resin is a condensation product of Bisphenol A and epichlorohydrin (see Chapter 10 entitled, "Epoxy Resins in Coatings").



The acrylic solution polymer is made acid functional simply by incorporating acrylic or methacrylic acid into the backbone; when cured under suitable conditions, it reacts with the epoxide to form ester linkages between the two polymers:



An alternative reactant to epoxies based on Bisphenol A/epichlorohydrin is another acrylic polymer wherein epoxide sites have been incorporated by polymerizing glycidyl acrylate, glycidyl methacrylate, or allyl glycidyl ether into the acrylic backbone. This approach is limited in use, however, because both economics and performance favor the Bisphenol A type epoxides. Also, in recent years, epoxy manufacturers have developed many aliphatic epoxides in an attempt to mimic the benefits of the workhorse Bisphenol A based products (i.e., resistance properties) without the accompanying disadvantages (i.e., poor resistance to UV light).

The carboxyl-functional acrylic resins typically have a molecular weight in the 10 000 to 50 000 range and a carboxyl content of 5 to 20%. Some higher solids acrylics are lower in molecular weight with higher acid content. The acid content of the acrylic polymer determines the equivalent weight of epoxy resin required to react with the acrylic to achieve a thoroughly cross-linked system.

Styrene or vinyltoluene are often incorporated into the acrylic polymer as "honorary" acrylic monomers because their reaction kinetics with acrylic monomers are fairly good and because they often improve alkali resistance and are low in cost. The cross-linking reaction between the carboxyl group on the acrylic polymer and the epoxy resin is fairly sluggish and requires a base catalyst such as dodecyl trimethyl ammonium chloride, or tri(dimethylaminomethyl) phenol. In some instance, melamine-formaldehyde resins are sufficiently basic to be used as catalyst and have the additional advantage of entering into the cross-linking reaction [*13*]. For improved package stability, however, it is preferable to add the base catalyst to the other components just prior to use. Even with catalyst, the baking or stoving requirements for acid/epoxide systems are fairly high, with 15 to 30 min at 150 to 190°C being typical. Of course, the higher the bake temperature, the shorter the bake time required for cure. To determine the optimum conditions for a given system, it is best to cure that system at a variety of baking conditions and then measure properties to determine the temperature and time required for maximum performance.

The primary uses for acid-functional acrylics cross-linked with epoxy resin are as appliance enamels and coatings for interior metal furniture and equipment. Acrylic/epoxy enamels fill the needs of the appliance industry primarily because of their excellent alkali/detergent resistance [see ASTM Practice for Detergent Resistance of Organic Finishes (D 2248-89)], which is critical to the performance of washing machine coatings. Other properties that are important to the appliance industry include: hardness, scratch resistance, grease resistance, stain resistance, as well as flexibility, impact resistance, and adhesion to metal. Acrylic/epoxy enamels, on the whole, offer an excellent balance of these important properties. Typical properties for an enamel based on an acid-functional acrylic resin cross-linked with a Bisphenol A based epoxy are shown in Table 3.

The disadvantages associated with acrylic/epoxy coatings are usually concerns brought about by the aromatic nature of the Bisphenol A based epoxy cross-linker. Their most significant limitation is poor resistance to UV light, which restricts their use to interior applications. If used outside, the aromatic Bisphenol A portion of the epoxy would degrade rapidly, and early chalking would occur. In some of the newer high-solids acrylic/epoxies, the epoxy content is very high and can therefore cause discoloration problems even indoors due to UV light. Where this is a problem, an aliphatic epoxy can be substituted for at least some of the Bisphenol A based epoxy to reduce sensitivity to UV radiation (see Chapter 10 entitled "Epoxy Resins in Coatings").

Acrylic Polymers Cross-Linked with Amino Resins

Acrylic polymers containing acid or hydroxyl functionality can be cross-linked with amino resins such as: urea, melamine, and benzoguanamine formaldehyde condensates (see Chapter 8 entitled "Amino Resins") as follows:

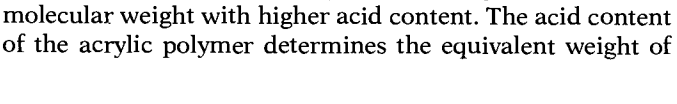


TABLE 3—Application properties for a white enamel based on an acid functional acrylic resin cross-linked with a Bisphenol A based epoxy [*14*] (baked 30 min at approximately 180°C).

Tukon hardness	16.2
Pencil hardness	2H
Solvent resistance, glass	
Cellosolve acetate, 15 min	6B
Cellosolve acetate, 60 min	6B
Xylol, 15 min	5B
Stain resistance, cold-rolled steel	
Mustard, 30 min	no stain
Ink, 30 min	trace
Print resistance, cold-rolled steel	
82°C, 30 min, 2 psi	light print
Detergent resistance[a]	
1% detergent, 74°C, 200 h	Few—6
Optical properties, CRS (two coats)	
Original 60° gloss	95.5
Gloss after 16 h at 178°C	95.4
Original color	9.2
Color after 16 hr at 178°C	13.0
Microknife adhesion, CRS "H" Value	22.8
Mandrel Flexibility[b] ½ in., ¼ in., ⅛ in.	
Cold-rolled steel	0-0-0
Bonderite 1000	0-0-0
Reverse impact, inch-lbs (Joule)	
Cold-rolled steel	22 (2.48)
Bonderite 1000	15 (1.70)
Direct impact, inch-lbs (Joule)	
Cold rolled steel	35+ (3.96+)
Bonderite 1000	50+ (5.65+)

[a]ASTM blister rating. A rating of 10 means no blistering, a rating of 0 means very large blisters, with intermediate ratings judged by ASTM photo standards.
[b]0 = no cracks; 9 = delamination.

$$\text{AMINO RESIN—NHCH}_2\text{OR} + \text{ACRYLIC—OH} \longrightarrow \text{AMINO RESIN—NHCH}_2\text{ O—ACRYLIC} + \text{ROH}$$

Reactions with amino resins containing an -NH-CH_2OH group are possible because this group differs from a simple alcohol in that it is far more acidic and reactive. Likewise, the methylol ether (when capped with alcohol) is more reactive than a conventional dialkyl ether. The curing condition required for acid functional acrylics cross-linked with amino resins is approximately 30 min at 150°C, while for an analogous hydroxyl functional acrylic, the reaction is more facile, requiring 30 min at 125°C with an acid catalyst [*15*]. Since the acid-methylol reaction is relatively slow, it allows significant self-condensation of the amino resin [*16*]. This detracts from the overall toughness and resistance properties.

The hydroxyl-functional acrylics are, therefore, favored over acid-functional polymers and are most often used in combination with a methylolated or butylated melamine-formaldehyde or benzoguanamine-formaldehyde condensate. Urea-formaldehyde condensates are less durable and have been found to have lower gloss and poorer chemical resistance. Hydroxyl functionality is incorporated into the acrylic polymer by copolymerizing monomers such as hydroxyethyl acrylate (HEA) or hydroxyethyl methacrylate (HEMA). This type of combination produces cross-linked acrylic/amino enamels with outstanding exterior durability, good hardness, and mar resistance, as well as excellent resistance to solvent attack. Acrylic/amino thermosetting enamels were, therefore, very successful in replacing the less durable alkyd/melamine systems in automotive topcoat applications, and general industrial finishing. Over the years, the automotive industry has relied heavily on this type of thermosetting acrylic because it offers the outstanding durability of acrylic lacquers but with better resistance to solvents and elevated temperatures. It also offers significantly higher application solids. Also, it does not require factory buffing to achieve high gloss as do the acrylic lacquer coatings.

Another reason that acrylic/amino resin technology became so popular is because of the versatility of the chemistry, whereby properties can be readily altered by varying acrylic T_g, acrylic monomers, acrylic functionality level, and cross-linker type and level. This is very important in general industrial finishing, where coatings often must be custom tailored to the specific end use. Table 4 briefly demonstrates the kinds of variation in performance which can be obtained by a few manipulations in composition [*17*].

An alternate approach to a thermosetting acrylic polymer is to prepare an acrylic polymer which contains functionality analogous to a melamine/formaldehyde condensate. Methylol or methylol ether groups can be attached to an acrylic backbone, and the resulting polymer can self-condensate, resulting in a cross-linked structure without the need for an external cross-linking agent. Initially, an acrylic polymer is made containing acrylamide (AM). The polymerization is usually a conventional free-radical, solution polymerization carried out in alcohol or a combination of alcohol and aromatic solvent. As in most thermosetting acrylic polymers, mercaptan is usually included to control molecular weight. After the polymerization is complete, the polymer is treated with formaldehyde to convert it to the methylol amide. An acid catalyst will bring about etherification with the alcohol present, usually butanol. The conversion proceeds as follows [*18*]:

$$\text{POLYMER—CO—NH}_2 + \text{HCHO} \longrightarrow \text{POLYMER—CO—NH—CH}_2\text{OH}$$

$$\text{POLYMER—CO—NH—CH}_2\text{OH} + \text{ROH} \longrightarrow \text{POLYMER—CO—NH—CH}_2\text{OR} + \text{H}_2\text{O}$$

As an alternative process, the AM monomer can be methylolated before being polymerized. The finalized methylolated amide acrylic polymers condense readily when acid catalyzed at bake conditions of 30 min at 150°C. The condensation process is a two-stage reaction [*19*]:

$$2\ \text{POLYMER—CO—NH—CH}_2\text{OH} \longrightarrow \text{POLYMER—CO—NH—CH}_2\text{—O—CH}_2\text{—NH—CO—POLYMER} + \text{H}_2\text{O}$$

TABLE 4—Compositions, viscosities, and film properties of HEMA-based copolymers containing a variety of other monomers[a] [17].

	Acrylate Styrene	Methacrylate Styrene	Methacrylate Methyl Styrene	Methacrylate Ethyl Styrene
		Copolymer Composition, % by wt		
HEMA	27.5	27.5	27.5	27.5
BA	22.5	...	...	...
BMA	...	22.5	22.5	22.5
St	50.0	50.0	...	...
MeSt	...	...	50.0	...
EtSt	...	...	...	50.0
Viscosity in 1/1 xylene/butanol	U-V	W+	X+	X+
Solids content, % by wt	47.8	49.4	49.4	48.3
Cross-linking agent, % by wt[b]	30	30	30	30
		Film Properties		
Color or yellowness factor[b]				
Initial	−2.4	−4.6	−5.2	−3.0
After 4 h/219°C	6.2	−0.9	0.6	10.1
Gloss (60°), initial	98	98	94	98
After 4 h/219°C	84	92	84	74
Front impact, in./lb to fail	2	0	0	0
Flexibility, ⅛-in. mandrel	0	0	0	0
Knife scratch	7+	7	7	7
Resistance to:				
20% NaOH, 12-day exposure	10	10	10	10
50% HAc, 7-h exposure	10	10	10	10
Butyl acetate, 4-h exposure	6	10	10	3
0.5% Rinso at 74°C, blisters after 4 days of immersion	9−	9	9	9

[a]All copolymers were <1 in Gardner Holdt color. Films baked for 30 min. at 149°C. Ratings: 10 = best or no failure; 0 = complete failure.
[b]Butylated benzoguanamine formaldehyde.
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$$\text{POLYMER—CO—NH—CH}_2\text{—NH—CO—POLYMER} + \text{H}_2\text{O} \xrightarrow{\text{further heat}}$$

If the methylolated amide has been etherified by butanol capping, instead of water as a by-product, a mixture of butanol and dibutyl ether would be obtained. These types of self-condensing acrylic resins will also react with amino resins, but usually there is no justification for so doing (i.e., no improvements in performance). The strength of the methylol amide acrylics is that they have no glaring weaknesses and make very good general-purpose resins.

Isocyanate-Reactive Acrylics

Acrylic solution polymers that are cross-linked with isocyanates (often referred to as acrylic urethanes) are unique among the various cross-linking systems because they cure under ambient conditions—they don't require baking. The isocyanate group (—N=C=O) is extremely reactive and will cross-link with any type of functionality having a labile hydrogen atom. This includes amines, alcohols, ureas, urethanes, carboxylic acids, and amides. Acrylic polymers designed to be cross-linked with isocyanate resins generally contain hydroxyl functionality incorporated by polymerizing hydroxyethyl acrylate (HEA) or hydroxyethyl methacrylate (HEMA) into the acrylic backbone.

There are six basic types of curing mechanisms for urethane coatings [see ASTM Terminology Relating to Paint, Varnish, Lacquer, and Related Products (D 16-75)]. The two-package polyisocyanate/polyhydroxyl coatings make up "Type V." Of this class, acrylic urethanes based on weather-resistant hydroxyl functional acrylics predominate. The hydroxyl functional acrylic reacts with isocyanate resin as follows:

$$\text{ACRYLIC—OH} + \text{R—N=C=O} \longrightarrow \underset{\text{(a urethane)}}{\text{R—NH—COO—ACRYLIC}}$$

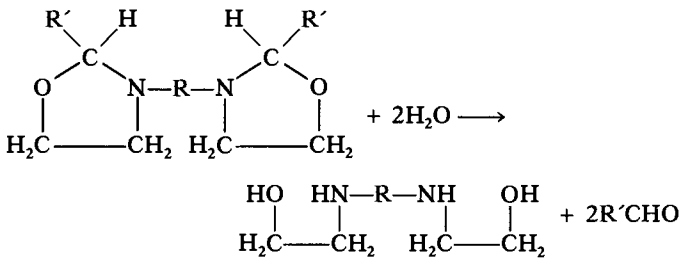
The preferred isocyanates are usually aliphatic, such as the adduct of hexamethylene diisocyanate (HMDI), because of the poorer color and exterior durability associated with the aromatic types of isocyanates. While the aromatic varieties of isocyanate react faster than the aliphatic types, a wide range of catalysts are available which can be used to speed up the cure of aliphatic isocyanates. A few such catalysts include triethylene diamine, zinc naphthenate, and dibutyl tin-dilaurate [20].

Acrylic solution polymers cross-linked with aliphatic isocyanates are ideal for applications where a durable, high-performance coating is required but where baking is not feasible because of the size or temperature sensitivity of the object to be coated. Acrylic urethanes are, therefore, invaluable in the transportation industry where high-quality coatings are needed for aircraft, railroad cars, trucks, buses, etc. Automobile refinishing, heavy equipment coatings, and high-performance maintenance coatings are also areas where acrylic urethanes are appropriate. The acrylic urethanes combine the inherent UV resistance and exterior durability of acrylics with the ambient cross-linking ability of aliphatic isocyanates to produce hard, tough, chemical-resistant, high-performance coatings. The major drawback of acrylic urethanes is that they are a two-package system and cannot be mixed until ready for application because they are so reactive and have a short "pot life."

Over the years, the hydroxyl-functional acrylics have been improving in performance, and now the emphasis is on higher solids content for lower VOCs. To meet more stringent VOC regulations, lower-molecular-weight, higher-solids hydroxyl functional acrylics have been developed. Increasing

the solids of the acrylic reduces solvent levels in the formulated coating. To compensate for lower molecular weight, one way to improve performance is to increase hydroxyl content, which in turn requires higher levels of isocyanate.

An alternative approach to reduced solvent or higher solids is to modify the acrylic urethane with a reactive diluent which is fluid and acts like a solvent but then reacts to form part of the cross-linked network [*21*]. One such diluent is a low-molecular-weight, difunctional oxazolidine which is non-reactive with isocyanates until ambient moisture opens the ring, releasing both hydroxyl and amine functionality [*22*].



This type of functionality has the advantage that it is one package stable with isocyanates as long as moisture is excluded from the paint. Because it has four reactive sites per molecule, it increases cross-link density for maximum performance, while it decreases solvent emissions.

ACRYLIC EMULSION POLYMERS

An acrylic emulsion is a two-phase system in which acrylic polymer droplets are dispersed in an external water phase, usually with the aid of an emulsifier (i.e., surfactant). Unlike some polymer emulsions, such as alkyds or epoxides, which are emulsified as preexisting resins, acrylic emulsions are made by an emulsion polymerization process wherein the monomer droplets are emulsified in water and then polymerized. A typical acrylic emulsion polymerization recipe is given in Table 5 [*23*].

The physical chemistry of acrylic emulsion polymers is much the same as for their solution polymer analogs, and the film properties of the emulsions can be controlled by manipulating polymer composition and molecular weight just as with acrylic solution polymers. However, the viscosity of an emulsion is unaffected by polymer molecular weight since solution principles do not pertain to emulsions (the polymer is insoluble in the continuous water phase). Therefore, for the best possible physical properties, the molecular weight of acrylic emulsions is generally higher than that of acrylic solution polymers: 100 000 to 1 000 000 for an emulsion versus 75 000 to 100 000 for a solution polymer.

The particle size of an emulsion is also very important in determining performance and must be carefully controlled. For example, the film-forming ability of an emulsion, as well as its pigment binding capability, is dependent on particle size, with smaller particle size being better than large particle size. Particle size does affect emulsion viscosity, with large particle size generally being associated with low viscosity.

TABLE 5—Copolymerization of ethyl acrylate, methyl methacrylate, and methacrylic acid [*23*].

Materials:

375.0 g	Deionized Water
5.1 g	Surfactant
100.0 g	Ethyl acrylate (15 ppm MEHQ)
100.0 g	Methyl methacrylate (25 ppm MEHQ)
4.0 g	Glacial methacrylic acid (100 ppm MEHQ)
4.0 mL	Ferrous sulfate solution (0.15%)
1.0 g	Ammonium persulfate in 5 mL of water
0.7 g	Sodium formaldehyde sulfoxylate in 5 mL of water
5 drops	t-butyl hydroperoxide (70%)

Procedure:

In a beaker, stir the surfactant with the water until dissolved and adjust the pH to 9.0 by adding 50% sodium hydroxide solution. Transfer this solution into the reaction flask, rinse the beaker with a small amount of deionized water, add the monomers and ferrous sulfate, and stir 15 min with flow of nitrogen before adding the initiators. The maximum temperature of 77°C is attained in 12 to 15 min. Stir 15 min after adding the initiators, then cool to room temperature, adjust to pH 9.5 with 28% aqueous ammonia, and filter; the gums amounted to 0.17%.

The free acid (unneutralized) surfactant can also be used as an emulsifier for the above copolymerization. In this case, the period of purging with nitrogen after charging the monomers should not exceed 15 min before the addition of initiators to avoid the formation of polymer emulsion product with excessive viscosity. Filtration of the finished emulsion gave only 0.05% gums. The properties of these emulsions were:

Surfactant Form	Sodium Salt	Free Acid
Solids Content, %—Calculated	35.0	36.0
—Found	34.3	35.6
pH at 25°C	5.6	1.8
Viscosity (Brookfield), cP	7.9[a]	10.5[a]
Particle size (light scattering), %	22.8[b]	12.3[c]
Minimum film-forming temperature, °C	22[a]	30[a]

[a]Emulsion adjusted to pH 9.5 before measurement.
[b]Measurement at 2% solids.
[c]Measurement at 0.4% solids.

Acrylic emulsion polymers (also known as acrylic latexes) have long been a mainstay of the architectural coatings market, particularly in exterior paints where their outstanding durability is so important. However, in recent years, clean air regulations have further strengthened the position of acrylic emulsions, usually at the expense of solvent alkyds. The use of acrylic emulsions in industrial coatings applications has also grown as a result of solvent emission restrictions. At the same time, the properties of acrylic emulsion polymers in the industrial coatings market has improved so that they now offer performance similar to their solvent-borne counterparts.

Acrylic Emulsions for Architectural Coatings

Architectural coatings are generally considered to be coatings intended for on-site application to residential, commercial, or institutional buildings; they are also known as trade sales coatings. Over the last 40 years, this market has evolved from an entirely oil-based market to one dominated by emulsions. There are three underlying reasons for the takeover of the architectural coatings market by emulsion polymers. The health, safety, air quality, and odor concerns associated with the solvents in oil-based paints have moved people towards

water-based latex paints whenever there is not a large penalty in performance. Also, latex paints are more tolerant of a wide variety of application conditions and can even be applied over damp substrates. Thirdly, emulsion polymers, particularly quality acrylic emulsions, have surpassed oil-based paints for long-term performance and protection in most applications.

Although acrylic emulsions generally provide a superior level of performance, their cost is somewhat higher than lower-performance emulsions such as vinyl acetates. Therefore, in segments of the architectural coatings market where performance is not critical, such as for interior flat paints, acrylic emulsions are not a dominant binder. However, in segments where performance and durability are essential, such as for exterior flat and gloss paints, acrylic emulsions control a very large portion of the market both in the United States and abroad.

Interior Coatings Applications

The high-volume, interior-flat market is dominated by vinyl acetate copolymers plasticized with a soft acrylate monomer, usually butyl acrylate at about the 15% weight level. Interior flat paints are aimed primarily at broadwall applications. Performance requirements for this market are fairly modest, with decorative features such as color, sheen level, and hiding being the more influential factors determining consumer preference. The one resistance property demanded in this market is scrub resistance; in this regard, vinyl/acrylics perform satisfactorily.

There is a small, premium segment of the interior flat market occupied by all acrylic latexes, and one of the key features which they offer is improved rheology and application characteristics resulting from the better interaction of acrylic latex particles with the new associative thickeners. Associative thickeners (also referred to as rheology modifiers) dramatically enhance flow, brushability, film build, and spatter resistance compared to conventional hydroxyethyl cellulose (HEC) thickeners.

Since interior flat paints contain a high pigment loading to increase hiding and reduce cost, the acrylic polymers used in this market tend to be fairly soft with good binding capacity. Typically, they are copolymers of a hard methacrylate monomer such as methyl methacrylate with a soft, commercially available acrylate monomer such as ethyl acrylate, butyl acrylate, or ethylhexyl acrylate. The T_g is generally around 10°C.

Interior gloss and semigloss paints have much more demanding requirements than flat paints since they are used for more diverse and challenging substrates such as windows, cabinets, and doors. Acrylic emulsions play a major role in this market, especially at the high-performance end. They are tailored to the specific needs of this market by optimizing the important variables contributing to performance: composition, hardness, molecular weight, and particle size.

Acrylic emulsions used in gloss and semigloss paints are copolymers of acrylate and methacrylate monomers and are usually harder than emulsions used in flat paints. They generally have a T_g in the range of 20 to 50°C. The harder polymers are necessary to build in block and print resistance, which are needed to keep doors and windows from sticking and to prevent marring and film damage associated with softer polymers. Since gloss and semigloss paints are formulated at low pigment volume concentration (PVC) to obtain gloss, the pigment does not contribute significantly to film hardness; it must all come from the polymer.

Since these gloss and semigloss latexes are often used over old oil-based enamels, adhesion to aged oil-based paints is required. This may be accomplished by copolymerizing adhesion promoting functional monomers into the acrylic polymer backbone. A major breakthrough in latex adhesion technology came about with the development of ureide functional acrylic monomers [*24*]. The adhesion promoter particularly is needed to improve adhesion and blister resistance when the paint film becomes wet, as it might in a bathroom. Since the gloss paints are often used in wet areas such as a bathroom, the water resistance of the dry film is also an important property. To ensure good water resistance, acrylic emulsions used in this market often contain hydrophobic monomers such as styrene.

Since interior trim paints are so highly visible, overall appearance properties are critical to the success of the paint job, and features such as flow and levelling, gloss, and film build are expected to be similar to oil-based enamels. This level of outstanding appearance has been possible in recent years with the introduction of associative thickeners. The traditional thickener for latex paints has been hydroxyethyl cellulose (HEC), which thickens by a flocculation mechanism and usually produces poor flow and gloss. Associative thickeners loosely bind to the surface of the latex particles through hydrophobic interactions, forming a network structure which accounts for their thickening action. The degree of interaction between the thickener and the latex particle is largely a result of the surface chemistry of the emulsion particles. Smaller particle-size emulsions have greater surface area and therefore have more interaction with associative thickeners. More hydrophobic latexes have stronger association with the new thickeners. Consequently, small-particle-size, hydrophobic acrylic emulsions have been designed specifically for use with associative thickeners. These newer acrylic emulsions optimize thickener interaction and produce exceptional flow and gloss. In fact, before these new emulsion/thickener systems, truly high-gloss latex paints were out of the question. They also improve brushability and film build, while eliminating the problem of roller spatter. Overall, the appearance properties of the newer small particle-size hydrophobic acrylics, when used in combination with associative thickeners, rivals that of oil-based enamels.

In an effort to further improve the performance of acrylic emulsions, the morphology of emulsion particles has become an additional important variable. In the past few years, new composite acrylic emulsions have been introduced, particularly into the interior gloss area, which are made up of two or more nonhomogeneous phases. They are prepared by a two-stage polymerization process sometimes referred to as a sequential emulsion polymerization that results in various types of core-shell structures. The goal of this type of polymerization is to incorporate the best characteristics of the different phases.

The hard acrylic emulsions typically used in interior gloss paints provide excellent performance but require considerable amounts of coalescent to achieve film formation (i.e., 10 to 20% by weight on polymer solids). This is undesirable both

from a cost and an organic emissions perspective. Using a two-stage polymerization, it is now possible to make hard, block-resistant acrylic emulsions that are also flexible and require lower coalescent levels. This type of polymerization can also be used to achieve a desired surface chemistry while not disturbing the bulk composition of the latex particle. This can be useful in optimizing rheology or improving adhesion characteristics of an acrylic latex.

Exterior Coatings Applications

By far the most challenging application for any coating is as an exterior paint required to protect a multitude of substrates in diverse and extreme weather conditions. It is in this demanding role that acrylic emulsions have met virtually all requirements and impressed the industry by their outstanding durability. One primary reason for their success, as mentioned earlier for solution acrylics, is their lack of absorption of ultraviolet light coupled with their inherent hydrolysis resistance. Over the years, acrylic emulsions have evolved from simple polymers troubled by shortcomings, such as poor adhesion or low film build, to sophisticated systems incorporating elements designed to address essentially every major challenge experienced by an exterior paint.

One of the toughest demands facing exterior flat house paints is the need to withstand the freeze-thaw type of expansion and contraction of dimensionally unstable substrates such as pine or other soft woods. To avoid the grain cracking that often occurs over this type of substrate, acrylic emulsions designed for flat house paints are fairly soft, with a T_g in the range of 10 to 15°C. A coalescing solvent is usually used in the formulation to assist film formation, particularly at lower temperatures. When the coalescent leaves, the acrylic paint film remains pliable and able to withstand substrate swelling and freezing, unlike oil-based house paints which become harder and embrittle on exposure as they continue to cross-link. The primary concern with making the acrylic polymer too soft is that dirt pickup would worsen. Since flat house paints contain a fairly high pigment content (i.e., PVC = 40 to 60%), dirt resistance is enhanced by the pigment loading. Experience over many years indicates that a T_g of 10 to 15°C is the optimum range to balance grain-crack resistance with dirt resistance.

For exterior flat house paints, the inclusion of an effective adhesion promoter in the acrylic backbone is crucial for good adhesion. The adhesion promoter greatly improves blister resistance. Furthermore, the improved adhesion enhances crack resistance over dimensionally unstable wood substrates. Painting over a degraded chalky surface is a common practice that can be a potential disaster if sufficient adhesion is not obtained. The chalk acts like a powdery barrier, preventing the emulsion binder from penetrating to the real substrate and establishing an adhesive bond. Studies have shown that smaller particle-size acrylic emulsions are much more effective than larger particle-size emulsions for filtering down through the chalk and obtaining adequate adhesion. For this reason, many exterior grade acrylic emulsions have been designed at a fairly small particle size of about 100 nm [*25*].

Small-particle-size, large-surface-area emulsions, when thickened with HEC, have poorer flow and film build than larger particle-size emulsions, which are less aggregated by the flocculating mechanism of HEC. Therefore, 100-nm emulsions that were designed to have improved chalk adhesion sacrificed some of the flow and film build of large particle-size (500-nm) emulsions. In an attempt to combine these seemingly mutually exclusive properties, particle-size distributions have been carefully controlled to ensure a tailored mixture of small particles that give good adhesion to chalky surfaces and large particles that help to improve flow in formulations thickened with HEC. An additional benefit of these polymers is their high supplied solids, which may be as high as 60% by weight compared to 40 to 50% for unimodal latexes.

Wide particle-size distribution acrylic emulsions do not significantly address the low film build associated with smaller particle-size emulsions when thickened with HEC. Film build is particularly important to an exterior paint because the durability of the film is usually proportional to the film thickness, i.e., how much paint is applied to the substrate. This was addressed in the 1980s by the Rohm and Haas Co. with the introduction of a Multilobe® acrylic emulsion, shown in Fig. 2 [*26*]. This type of polymer has a lobed morphology that is grown out during the polymerization process; it does not result from particle aggregation. The lobes of this polymer are about 350 nm, but it has an effective hydrodynamic volume of about 1000 nm and is, therefore, very effective at imparting high film build in paints thickened with HEC. It also reduces the level of thickener needed to achieve a given viscosity. Since in its commercial form this technology also contains small particles, good adhesion characteristics are retained while film build is optimized.

Other important aspects of weatherability are color retention and resistance to chalking. These properties are made worse by the catalytic degradation effects of TiO_2 on the binder, so that high PVC flat paints are generally poorer than low PVC gloss paints. However, the inherent durability of the binder is still a controlling factor, and acrylic polymers have excellent resistance to sunlight and erosion, which contribute to their very good chalk resistance and color retention. Among the common acrylic copolymer compositions in use commercially, MMA/BA polymers are better than MMA/EA polymers, and higher methacrylate containing binders are

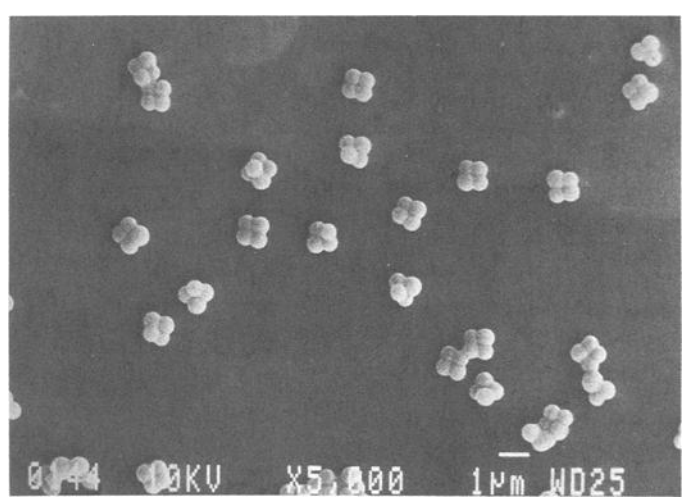


FIG. 2–Scanning electron micrograph of Multilobe® acrylic particles (courtesy of Rohm and Haas Co.).

better than acrylics containing higher levels of acrylate monomers. Of course, the methacrylate/acrylate levels are generally determined by the T_g required to achieve the desired balance of crack resistance and dirt pickup.

Exterior gloss and semigloss paints are required to withstand similar tortures as their flat paint counterparts and, in addition, must provide equally good dirt resistance at much lower pigment loadings. Acrylic emulsions have been designed that meet all of these challenges and perform very well in environments as diverse as the tropical regions of Asia and the Philippines to the Scandinavian regions of Europe. Since the acrylic emulsion engineered for interior gloss/semigloss paints are intended to be high-performance systems capable of good adhesion even in wet areas, they are often able to be used outside as well. Since exterior gloss paints must have good dirt resistance at low PVC, the acrylic emulsions used in these paints are harder than those used in flat paints and generally have a T_g in the area of 20 to 35°C. This T_g range can provide acceptable dirt resistance while still having good grain-crack resistance. The very hardest acrylic emulsions used for interior gloss paints (i.e., above T_g 35°C) would not be appropriate outside, at least in areas subject to freezing, because they would be more prone to grain crack.

Since brush marks are much more obvious in a gloss paint than in a flat paint, good flow and levelling is much more critical for a gloss paint than for a flat paint. Consequently, older acrylic emulsions intended for semigloss paints (there were no high-gloss latex paints until about 1980) are of large particle size to have the best possible flow with the prevailing thickener of the day, HEC. The flow of these systems could best be described as fair, but overall they have demonstrated an admirable balance of properties and are still popular today. However, newer acrylic emulsions intended for exterior gloss paint applications, particularly those generally referred to as acrylic enamel vehicles, are small in particle size (i.e., 100 nm) to take advantage of the excellent flow, gloss, and rheology available by using associative thickeners.

Over the past ten years, the decorative as well as protective capabilities of exterior gloss paints have improved significantly to the point where acrylic emulsions are rapidly replacing alkyd enamels as the preferred coating for exterior trim.

Acrylic Emulsion Maintenance Coatings

Maintenance coatings differ substantially from decorative coatings since they are used primarily for their protective features, which prevent substrate deterioration by corrosive elements. Maintenance coatings are generally used to protect metal surfaces such as bridges, storage tanks, and other industrial facilities, often in harsh chemical and corrosive environments. The first acrylic latex binders for corrosion-resistant maintenance coatings were introduced commercially in 1964. They are similar in hardness and composition to exterior flat house paint binders with the exception that they are formulated with reactive pigments and additives which help prevent rusting. The surfactants and other "salt and pepper" ingredients used in the polymerization of maintenance acrylic emulsions are carefully selected so as to not aggravate corrosion.

These acrylic latex maintenance coatings had the usual advantages in application of water-based paints over solvent alkyd paints along with expected advantages in chalk resistance, color retention, and other decorative qualities. However, to the surprise of some segments of the maintenance industry, acrylic maintenance emulsions often outperformed solvent alkyds for corrosion resistance and overall metal protection. This is partly because the alkyds continue to harden and eventually crack, leaving the substrate exposed and subject to the elements. Acrylic emulsions do not continue to harden once the paint film is dry, and they remain sufficiently pliable to expand and contract with the substrate.

The one weakness of the acrylic latexes in the area of maintenance coatings was their low T_g, which reflected a lower hardness than the alkyd paints. This limitation was removed by the development of aqueous gloss enamel binders. These hard latex binders used in interior and exterior gloss paints were fine tuned to maximize corrosion resistance and overall protection. Commercialized in the mid-1980s, this new generation of maintenance vehicles has proved very successful in extensive field tests, particularly on bridges in the southeastern United States. The small particle size of these binders fits perfectly with associative thickener technology to give tight water-resistant films, which are an improvement over HEC-thickened paints that can have microscopic defects as a result of the flocculating mechanism of HEC [27].

Acrylic Emulsions for Industrial Coatings

Nonreactive Emulsions

Industrial coatings users, who have traditionally applied solvent-based polymers, have recently been under pressure to reduce volatile organic emissions. This is particularly true in California, which has historically been at the forefront of clean air legislation. In many instances, these coatings users have complied with the stricter environmental legislation by switching over to water-based systems. Acrylic producers have responded to the needs of these coatings users by developing more sophisticated emulsions capable of meeting the demanding performance requirements of many different end users. Early emulsions aimed at industrial coatings applications were offshoots of architectural coatings technology and were often too soft for industrial coatings uses. Also, high gloss was not possible with these older emulsions. Like the newer gloss enamel emulsions for trade sales use, however, latexes aimed at industrial coatings applications have evolved into hard, resistant binders that match the performance of their solvent-based counterparts. Without this evolution in performance, it is unlikely that industrial coatings users would switch to latex coatings even with the more severe emissions regulations.

Thermoplastic acrylic emulsions designed for industrial coatings applications generally have to be harder and faster drying than architectural emulsions and have better corrosion and chemical resistance. The typical T_g range for such acrylics is about 30 to 70°C. The film formation problems usually associated with such hard emulsions are somewhat alleviated by the controlled application conditions in the factory, so that low-temperature film formation is generally not required. For general industrial finishing over metal substrates, industrial acrylic emulsions have borrowed technology from maintenance finishes and have optimized sur-

factants, additives, and compositions to improve rather than detract from corrosion resistance.

Newer heterogeneous acrylic emulsions comprised of two or more phases have recently become important in the industrial coatings industry. One such type of heteropolymer, the core-shell polymer, is being used to achieve rapid hardness development with improved block and print resistance at low VOC. These properties allow the manufacturer to stack, pack, and ship coated parts more quickly [*28*]. Using core-shell technology, acrylic emulsions have been able to rival the performance of traditional, high-solvent-content nitrocellulose lacquers in wood coatings and furniture finishes. The major deficiency of acrylic emulsions in these areas is the "warmth" of water-based coatings compared to solvent-based materials. "Warmth" is a quality which refers to the feel and appearance of the coated wood.

Thermosetting Emulsions

Just as is the case with solution acrylics, functional groups can be incorporated into the polymer backbone of an acrylic emulsion so that it can react with another functional material after application to the substrate, forming a cross-linked polymer. Typically hydroxyl or hydroxyl/acid functional acrylic emulsions are cross-linked with urea or melamine resins. Acid functional acrylic emulsions can be cross-linked with emulsified epoxy resins. The chemistry of these systems is identical to the cross-linking chemistry discussed earlier for solvent-based acrylic resins. After the emulsion is cross-linked, the infinite molecular weight provides for solvent and chemical resistance, along with hardness and toughness. By adjusting the level of functionality, the amount of cross-linker, and the T_g of the acrylic emulsion, a system can be custom designed for a specific application.

For many years, the construction industry has relied on hydroxyl functional acrylic emulsions reacted with urea or melamine to coat products such as hardboard, wood panels, shingles, and metal coil. In interior applications, such as over wood paneling, these emulsions offer comparable cure speed and performance to solvent-based alkyd/urea systems. In coil coating applications, the thermosetting acrylics offer high gloss, excellent durability, good corrosion protection, as well as good roll coatability. These emulsions have been applied at line speeds up to 137 m/min with good transfer, flow, and leveling. Usually these systems are catalyzed with an acid catalyst to achieve the fastest/lowest temperature cure. A very good property balance is demonstrated in Table 6 for an aqueous acrylic melamine coil coating enamel [*29*].

A recent development in cross-linking acrylic emulsion technology is an epoxy cross-linking, ambient cure system which has many applications but has been found to be particularly useful in maintenance coatings. Besides being ambient curing, an attractive feature of this system is its excellent early properties resulting from the high-molecular-weight acrylic emulsion, which provides ample resistance characteristics until the epoxy cross-linking is complete. This new acrylic/epoxy system is compared to an epoxy/polyamide

TABLE 6—Properties for an aqueous acrylic/melamine coil coatings enamel over aluminum and galvanized steel [*29*].

Substrate	Aluminum[a]	Mini-Spangle Galvanized Steel[a]
Primer thickness	0	0.2
Topcoat film thickness	0.9 to 1.0	0.8
Gloss 20°/60°	65/89	−/80[b]
Image clarity	Very good	Good
Tukon hardness (KHN)	9	9
Pencil hardness		
Initial	H	H
Wet 16 h, 38°C, H_2O	B	B
Flexibility—X30 microscope	2-3T	3T
Direct impact, in.-lbs	20 to 25	35
Reverse impact, in.-lbs	15	10
Metal mark resistance	Excellent	Excellent
Rheology	Excellent	Excellent
MEK rubs	200	200
Cleveland condensing cabinet, 200 h at 60°C	Pass	Pass
After 1000 h Salt Spray Exposure		
X-scribed area		
Tape adhesion, % removed	0	0
Lifting	None	None
Undercutting	1/16 in.	1/16 in.
Blistering[c]	None	Mod-Dense, No. 6, No. 8
Exposed edge		
Undercutting	...	4/16 in.
Blistering[c]	...	Mod, No. 2, No. 4
1/8-in. mandrel bend		
Blistering[c]	...	None
White rust	...	None
Flat		
Blistering[c]	None	None

[a]Commercial chromate pretreatment.
[b]Gloss dependent on smoothness of substrate.
[c]1-9: Higher numbers indicate smaller blisters. Blister density is rated as few, moderate, or dense. 10 = no blisters.

TABLE 7—Resistance characteristics of acrylic/epoxy water-borne coatings versus conventional controls [*30*].

	3 Weeks, Air Dry		
	Acrylic/Epoxy Formulation	Epoxy/ Polyamide	Alkyd
Solvent Resistance			
MEK rubs to remove	>300	>300	120 Lifted
Spot tests, 15 min.			
MEK	Mod. soft	Mod. soft	Lifted
Toluene	Mod. soft	Mod. soft	Lt. soft
Butyl acetate	Lt. soft	Lt. soft	Lt. soft
Gasoline	Lt. soft	Lt. soft	Lt. soft
Butyl cellosolve	Lt. soft	Mod. soft	Mod. soft
Stain Resistance			
Spot tests, 24 h			
Mustard	OK	Lt. stain	Med. stain
Coffee	OK	OK	OK
Red ink	OK	Lt. stain	Hvy. stain
Cola	OK	OK	OK
Grape juice	OK	OK	OK
Acid/Base Resistance			
24-h immersion, on concrete			
HCl	No effect	No effect	No effect
NaOH	No effect	No effect	Dissolved
Accelerated Exposure, 300 h of QUV Exposure			
Gloss retention, percent	63	4	4
Fade resistance (green coatings)	Good	Very poor	Poor
800 h of Fade-O-Meter exposure			
Gloss retention, %	49	2	10

NOTE: Lt. = light; Mod. = moderate; Med. = medium; Hvy. = heavy.
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coating and an alkyd coating in Table 7 [*30*]. The strong points of the acrylic emulsion/epoxy system are its stain, solvent, and chemical resistance, along with outstanding weathering. No less a key feature is its very good corrosion performance [*31*].

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7

Alkyd and Polyesters

by Al Heitkamp[1] *and Don Pellowe*[2]

ALKYD RESINS, COMMONLY KNOWN AS "ALKYDS," are synthetic polymeric materials that have been used in the coating industry since the 1930s. Today they continue to be the "workhorse" polymers for the paint, coating, and printing ink industries. Alkyd and chemically modified alkyd polymers find use in most types of liquid organic coatings for architectural, air-dry, and baked industrial and maintenance coatings. Alkyds are a special class of polyesters that often have vegetable oil or fatty acids coreacted into the polyester, and these compounds provide the distinctive air-cure feature of many of these compounds.

Three major classifications of alkyds are those designed for conventional solids, higher solids, and water-borne coatings. Because there are a large variety of commercially available intermediates and chemical modifiers—i.e., monomers—for the preparation of alkyds, they continue to be the most versatile type of polymers for coatings and printing inks.

Most alkyds are film-forming polymers with a relatively low glass transition temperature (T_g), i.e., below 0°C. They are easily pigmented and readily accept additives to form coatings with a wide range of appearance, performance, and application characteristics. Alkyds are extensively used on wood, metal, plastic, composite, and other substrates such as primers, topcoats, maintenance paints, undercoatings, exterior trim paints, wall paints, and similar end uses.

Polyesters for coatings are based on a coreaction of polyhydric alcohols and polybasic acids. Such polyesters may be prepared from one or more polyhydric alcohols and polybasic acids to meet particular coating performance requirements.

HISTORY

Although condensation products of dihydric alcohols and dicarboxylic acids were known at the start of the 20th Century, alkyds modified with drying oils were developed in the late 1920s by Kienle et al. [*1–5*]. The early condensation products were not soluble in common solvents and did not air dry until monofunctional acid or fatty acids were incorporated into the polymeric material. Kienle coined the term "alkyd" from the alcohols ("al") and acids ("cid") used in their preparation. The early spelling of "alcid" was later changed to the current form, "alkyd." Air-dry films were the result of oxidative polymerization and cross-linking that took place through coreaction of oxygen and the carbon-carbon bond unsaturation part of the fatty acids. The use of vegetable oils and fatty acids as coreactants with the early developed polyesters was the technological breakthrough that led to alkyd resins being the predominate binder for organic coatings. Other developments contributed to the general interest in the products such as new techniques for the production of phthalic anhydride, synthetic glycerin, and other new, novel polyhydric alcohols.

Typically, an alkyd could be based on glycerin as the polyol, phthalic anhydride as the polybasic acid, and soya or linseed oil as the vegetable oil. These compounds are coreacted and then reduced with aliphatic or aromatic petroleum-based hydrocarbon solvents. Monofunctional fatty acids such as tall oil fatty acids or special blended fatty acids are commonly found in alkyds as alternatives to vegetable oils.

ALKYD SYNTHESIS, PROCESSING AND MANUFACTURE

Three major categories of chemical intermediates are utilized in the manufacture of alkyd resins:

- Polybasic organic acid/anhydride—example, phthalic anhydride
- Polyhydric alcohol—example, glycerin
- Monobasic fatty acid or triglyceride—example, soya fatty acids or soya oil

The stoichiometric proportions and the equivalent weight of these monomers lead to the desired physical properties and molecular weight distribution of the resulting alkyd. The solvent selection and quantities used influence the viscosity, nonvolatile content, and the solvent evaporation rate from coating films.

Alkyd processing is mainly a condensation reaction between hydroxyl and carboxyl groups of the chemical intermediates. The main by-product of the reaction is water, and it must be removed during the polymerization process or it will transesterify back into the alkyd and change characteristics. Other chemical reactions are possible during preparation, and these include dimerization of fatty acids or vegetable oils depending on their unsaturation and the alkyd processing temperature. Vegetable oils (triglycerides) are used for economical alkyd manufacture, whereas fatty acid blends are used in high-performance alkyds—particularly in higher solids and water-borne types.

[1]McWhorter Technologies, 1028 South Third Street, Minneapolis, 55415.
[2]Retired, formerly employed by Frost Paint.

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An alkyd resin can be modified with a number of intermediates. Some of the more common types are:

- Acrylates
- Benzoic acid
- Epoxides
- Isocyanates
- Paramethyl styrene
- Phenolics
- Polyamides
- Rosin
- Silicone
- Styrene
- Vinyl toluene

More than one of the above compounds are often used to impart particular characteristics when an alkyd is modified.

There are two major methods of preparing or processing alkyds for both laboratory and production scale. These methods are the fusion and solvent reflux processes.

Fusion Process

In this method of manufacture, the alkyd intermediates are charged into the reaction vessel. Then an inert gas, such as dry nitrogen or carbon dioxide, is introduced to "blanket" the vapor space above at the top of the reaction vessel. The reaction mixture is heated from 350 to 500°F (175 to 260°C). The main polymerization occurring is by condensation to form ester groups. Water of condensation exits from the top opening of the reactor. Vigorous mixing and agitation are required throughout the process to insure uniformity of the final resin (Fig. 1). The product provided by this process depends greatly on the procedure conditions followed in temperature and timely removal of water-of-reaction by-product.

Solvent Reflux Process

In the solvent reflux process, an azeotropic solvent such as xylene is commonly used in the reaction. The purpose of the azeotropic solvent is to aid in removal of water formed during the condensation reaction. The reflux solvent and water volatilize together and liquefy in a condenser placed above the reaction vessel. A separator or Dean-Stark trap below the condenser collects this liquid mixture, and the azeotrope solvent is returned to the reaction vessel (Fig. 2). The choice of azeotrope solvent affects the temperatures maintained during the reaction.

In both fusion and solvent reflux processes, acid number and viscosity are measured until the final desired values are

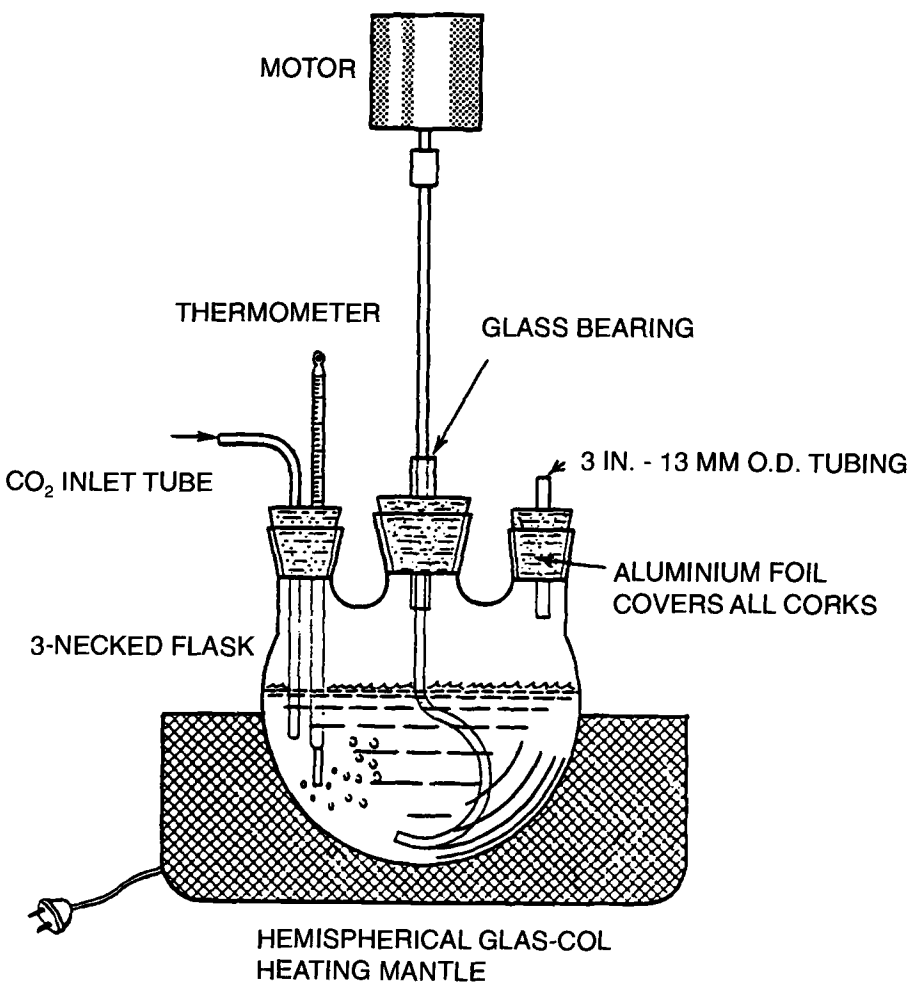

FIG. 1–Apparatus for fusion cooking of alkyds. (Diagram courtesy of ICI Hercules Alkyd Reports.)

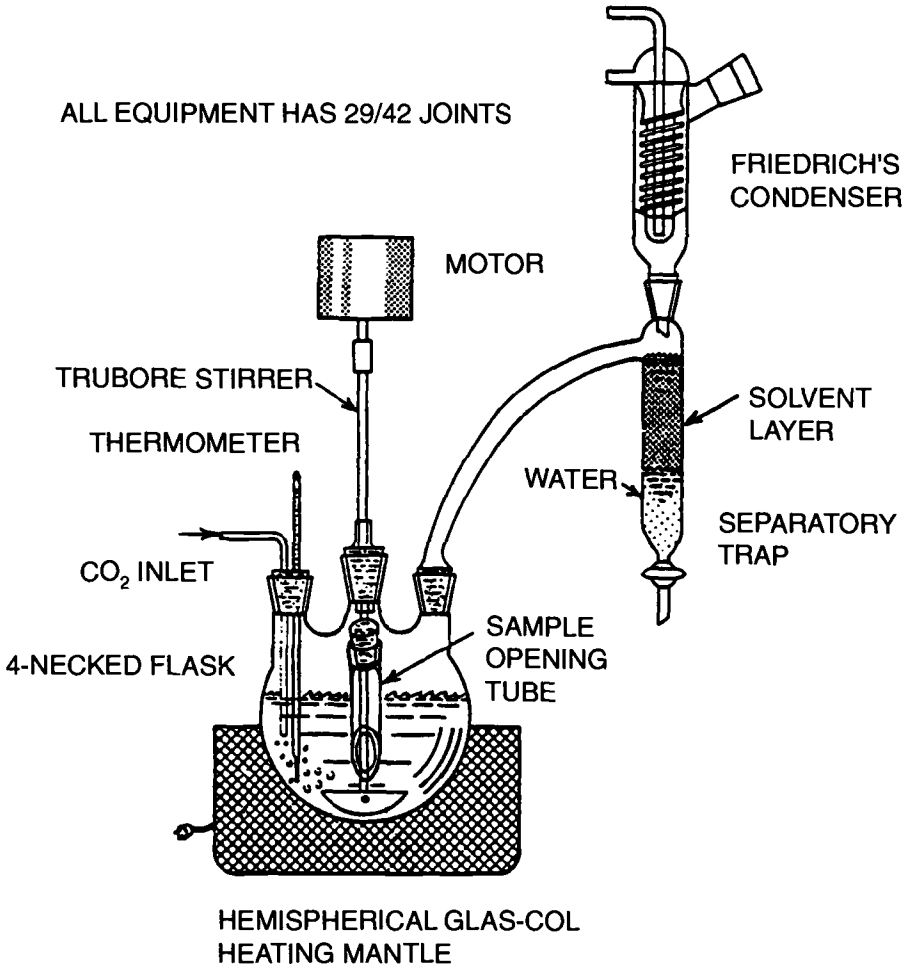

FIG. 2—Laboratory apparatus for solvent cooking of alkyds. (Diagram courtesy of ICI Hercules Alkyd Reports.)

reached. Then the alkyd is thinned with the desired type and amount of organic solvent. Only a small amount, usually less than 3% by typically 1% of the total weight, of the reflux or azeotrope solvent remains in the alkyd. The solvent reflux process advantages are less emission of by-products to the atmosphere and faster processing time. Also, a greater variety of alkyds can be made by this process. The final alkyd solution properties are measured at 25°C. Typical tests include color, acid number, hydroxyl number, hardness, viscosity, and percent nonvolatiles.

RAW MATERIALS (INTERMEDIATES) FOR ALKYD RESINS

Typical polybasic acids, polyhydric alcohols, and monobasic fatty acids or oils are given in Tables 1, 2, and 3. The numerous possible raw materials available and economic considerations of these lead to versatility of alkyds and to a wide range of commercially available products.

PHYSICAL PROPERTIES

The most common physical properties used to identify characteristics of alkyd resins are determined by ASTM methods.

Viscosity

The viscosity of alkyds covers a wide range and must be compared to the nonvolatile content and type organic solvent used, ASTM D 1545: Test Method for Viscosity of Transparent Liquids by Bubble Time Method [*6*]. The bubble tubes and measured times in seconds are easy to run with proper testing equipment and a constant temperature set at 25°C. Viscosity is important in reflecting alkyd molecular weight and the final coating application properties, thickness, and minimizing batch-to-batch variation of each specific alkyd. Relatively high-molecular-weight alkyds need to be reduced to application viscosity with a greater amount of solvent or solvent mixture or with solvents that have a particular solvency for the specific alkyd.

NONVOLATILE CONTENT

The nonvolatile content of alkyd solutions is determined with ASTM D 1259: Test Method for Nonvolatile Content of Resin Solutions. Alkyd specifications are designed to show a 1 or 2% variation from an agreed on nonvolatile by weight requirement. This method is sometimes varied to a higher oven temperature of 150°C and a shorter dwell time in resin processing use.

TABLE 1—Acids and anhydrides used in alkyd manufacture.

Polyfunctional
Adipic acid
Azelaic acid
Chlorendic anhydride
Fumaric acid
[a]Isophthalic acid
[a]Maleic anhydride
[a]Phthalic anhydride
Succinic acid
Sebacic acid
Citric acid
[a]Trimelletic anhydride
Monofunctional
Abiatic acid
[a]Benzoic acid
Caproic acid
Caprylic acid
Capric acid
Castor oil acids
Coconut oil acids
Cottonseed fatty acids
Lauric fatty acids
Linoleic acid
Linolenic acid
Oleic acid
Tallow acids
[a]Tall oil fatty acids
Tertiary-butyl benzoic acid
Special blended fatty acids

[a]Most commonly used in commercial alkyds.

Alkyd resin solutions vary from 30% nonvolatile (flat wall, medium-oil alkyds) to 100% nonvolatile content by weight (very long oil alkyds for exterior paints, stains, latex modifiers, and similar products).

Color

The color of alkyd solutions is determined by comparison with a range of color standards referred to as the Gardner-Holdt color standards, ASTM D 1544: Test Method for Color of Transparent Liquids (Gardner-Holdt Scale) [*8*]. The color or degree of yellowness of the alkyd solution may or may not have an effect on the color of the final coating films.

TABLE 2—Polyhydric alcohols used in alkyd manufacture.

Polyhydric Alcohols
[a]Glycerin
[a]Ethylene glycol
Propylene glycol
Trimethylol propane
[a]Neopentyl glycol
Hexylene glycol
Pentanediol
1,3-Butylene glycol
Diethylene glycol
Triethylene glycol
[a]Pentaerythritol
Methyl glucoside
Dipentaerythritol
Sorbitol
[a]Trimethylpentanediol
Trimethylol ethane

[a]Most commonly used in commercial alkyds.

TABLE 3—Vegetable oils used in alkyd manufacture.

Vegetable Oils
Castor oil
[a]Coconut oil
Corn oil
Cottonseed oil
Dehydrated castor oil
[a]Linseed oil
Safflower oil
[a]Soybean oil
Tung oil
Walnut oil
Sunflower oil
Menhadden oil[b]
Palm oil

[a]Most commonly used in commercial alkyds.
[b]A nonvegetable oil derived from fish.

Density

The density or specific gravity of alkyds is also referred to as the weight per gallon or density and can be determined by following ASTM D 1475: Test Method for Density of Paint, Varnish, Lacquer, and Related Products [*9*].

Flash Point

The flash point of alkyds is mainly of importance as it pertains to shipping the products and formulated paints, i.e., to bill of lading and other regulations. ASTM D 3278: Test Methods for Flash Point of Liquids by Setaflash-Closed-Cup Apparatus [*10*] is the most common test that will provide conformance with Department of Transportation regulations. However, other ASTM methods are utilized. The method utilized depends on flash cup availability and other specified requirements.

Neat alkyds have low vapor pressure. Therefore, the flash point of an alkyd solution reflects the flash point of the solvent used to dissolve the alkyd. It is recommended that flash points on alkyd solutions actually be measured by laboratory determination. The flash point of an alkyd solution is different from that of the actual solvent or solvents incorporated into the solution.

Drying Properties

The drying properties of alkyds are of importance when describing the product. Metallic driers are based on cobalt, manganese, iron, lead, calcium, and rare earths reacted with synthetic organic acids, such as vegetable fatty acids, to form soaps. When these driers are added to the alkyd-based coating, they act as catalysts and accelerate the rate of air drying and cross-linking. Driers are formulated in combinations or blends to maximize desired dry film surface and interior characteristics. In recent years, synthetic acid-based metallic driers have gained popularity for two main reasons: (1) higher metal concentration in the drier, and (2) greater uniformity of drier performance. Methods associated with determining drying are given in ASTM D 1640: Test Methods for Drying, Curing, or Film Formation of Organic Coatings at Room Temperature [*11*].

Acid Value

The free organic acid groups present in the nonvolatile portion of an alkyd resin is an important property for pigment wetting and performance properties of organic coatings. The acid value of alkyds is typically determined with ASTM D 1639: Test Method for Acid Value of Organic Coating Materials [*12*]. Reasonably accurate and consistent results can be obtained with this test procedure.

Hydroxyl Value

The hydroxyl value or number is a measurement of the free hydroxyl groups remaining in the alkyd that have not been reacted with carboxyl groups during the condensation stage of the alkyd resin preparation process. Hydroxyl value determinations are more difficult to perform than acid number determinations. There are several reasons for this. First, the hydroxyl group can be sterically hindered or less available within the polymer and thus difficult to reach with the reactants. Second, hydroxyl groups on primary carbon atoms are more reactive than those on secondary carbon atoms, and these are more reactive than those located on a tertiary carbon atom. Tertiary-positioned hydroxyl groups are the most difficult to esterify in this determination. Manufacturers can often specify methods that can be used for secondary hydroxyl groups.

Hydroxyl numbers are important in determining equivalent weight, which in turn is important to determining the amount of urea formaldehyde, melamine formaldehyde, or urethane prepolymer to react with the alkyd. In the case of oil-modified urethanes, also called uralkyds, the hydroxyl groups coreact with free isocyanate functionality. Although theoretical equivalency based on hydroxyl numbers is a good guideline to establishing performance characteristics, a ladder of co-reactant ratios is important to optimizing particular performance characteristics.

ALKYD RESIN CLASSIFICATION

Unmodified alkyds are classified into four types that depend on oil content—very long-oil, long-oil, medium, and short-oil alkyds. Properties such as speed of drying, ease of brushing, film flexibility, chemical resistance, and exterior gloss retention are all dependent on the oil content. These properties are summarized in Table 4.

A summary of alkyd resins comparing types of oil/fatty acids, nonvolatile, solvent, and typical application is given in Table 5.

TABLE 4—Alkyd resin properties related to oil length.

	Very Long Oil	Long Oil	Medium	Short Oil
Oil content	Highest	⟷		Lowest
Speed of drying	Slowest	⟷		Fastest
Ease of brushing	Best	⟷		Worst
Film flexibility	Highest	⟷		Lowest
Chemical resistance	Worst	⟷		Best
Exterior gloss retention	Worst	⟷		Best

HIGHER SOLIDS ALKYD RESINS

Higher solids alkyds have been developed to reduce organic solvent emissions in those applications under regulatory restrictive requirements. This is accomplished by the development of polymers with lower viscosities than so-called conventional alkyds. The design and processing of higher solids alkyds result in a lower average molecular weight than conventional alkyds. A narrower molecular weight range of the resin species is necessary to meet air-dry, nonvolatility, and performance properties of the coatings. Another important factor is solvent selection. Organic solvents with greater viscosity reduction of the base or neat alkyd are needed to lower coating hydrocarbon atmospheric emissions. The release of these solvents during coating film formation is an important consideration.

The higher solids alkyd resins are available in all classes of "conventional alkyds" such as those shown in Table 6.

Higher solids alkyds can replace their conventional solids counterparts in many coating applications, thus affording decreased atmospheric emissions. Such products are used in air-dry architectural enamels and both air-dry and baking industrial primers and topcoats.

WATER-BORNE ALKYD RESINS

Water-borne alkyds obtain their water reducibility by the use of coupling solvents and amine-neutralized carboxyl groups on the polymer. Typical coupling solvents are ethylene glycol monobutyether, propylene glycol monoethylether, propylene glycol monopropylether, and four-carbon alcohols such as s-butyl alcohol. Water-borne alkyds are available in most classes of "conventional alkyds" such as those shown in Table 7.

SATURATED POLYESTERS

Saturated polyesters are also called oil-free alkyds. The oil or fatty acid modification is zero percent, and this factor results in a polymer that cannot be air dried to a cross-linked coating. Rather, these polymers are formulated with a curing agent or cross-linker and baked. The curing agent can be a urea-formaldehyde or a melamine formaldehyde resin, both of which require baking. Polyurethane prepolymers can be coreacted with polyester resins for air-dry or low-bake coatings in two-component systems. In such systems, the saturated polyester provides the hydroxyl groups for cure with free isocyanate groups on the polyurethane prepolymer.

The physical properties of these coatings are outstanding due to the absence of fatty acids, and they afford coatings with excellent color retention, flexibility, exterior durability, and hardness.

The type of resins can be adapted to provide higher solids saturated polyesters by redesigning the polymer and using organic solvents with appropriate solvency rather than the customary blends of aromatic hydrocarbons with ketones, alcohols, and glycolethers.

Water-borne polyesters are available through design of polymers having acid numbers in the range of 40 to 60. When these products are neutralized with an amine, they become

TABLE 5—Description of unmodified alkyd resins.

Type Alkyd	Oil or Fatty Acid	Nonvolatiles	Solvent	Typical Applications
Very long	Linseed Soya Tall oil	85–100%	Aliphatic hydrocarbon	Exterior latex modifier House paint modifier Oil-based stain and ink vehicles and modifiers
Long	Linseed Safflower Soya Sunflower Tall oil acids	60–70%	Aliphatic hydrocarbon	Architectural coatings Maintenance coatings One-coat enamels Exterior enamels Primers Topcoats
Medium	Linseed Safflower Soya Sunflower Tall oil acids Blends	45–50%	Aliphatic hydrocarbon Aromatic hydrocarbon	Farm implements Railway equipment Maintenance
Short	Castor Dehydrated castor Coconut Linseed Soya Tall oil acids Blends	50%	Aromatic hydrocarbon or Rule 66-type solvent blend[a]	Industrial coatings

[a]A typical Rule 66 type solvent is isobutanol, VM&P naphtha, and xylene at 8% maximum volume solids. Rule 66 is a 1966 regulation from California's South Coast District that restricted the amount of aromatic hydrocarbon solvent in a coating formulation. In the 1960s, research indicated that these types of solvents contributed greatly to atmospheric ozone formation. Rule 66 legislation was adopted by many other local and state regulators.

soluble in blends of water and cosolvents and yield systems with low-volatile organic compound content. Formulation of a coating from these products involves the use of water-borne or water-tolerant ureas and melamines. The cured films offer excellent hardness, gloss, and flexibility.

TABLE 6—Higher solids alkyd resin types and end uses.

Type	Typical End Use
Long oil	Architectural enamels
Medium oil	Transportation enamels
Short oil	General industrial air-dry and bake enamels
Benzoic acid terminated	Implement enamels
Phenolic modified	Primers
Silicone modified	Maintenance topcoats
Copolymer	Aerosol enamels

TABLE 7—Waterborne alkyd resin types and end uses.

Type	Typical End Use
Long oil	Stains and enamels (limited package stability)
Medium oil	General industrial air-dry enamels
Short oil	General industrial baking enamels, automotive under the hood parts
Benzoic acid terminated	Implement enamels
Phenolic modified	Primers
Silicone modified	Maintenance topcoats

SILICONE-MODIFIED POLYESTERS

Conventional Types

Silicone modification of polyesters is accomplished by use of a silicone intermediate incorporated through reaction at a 30 and 50% level. The silicone intermediates are of either hydroxy or methoxy functionality, and when they are reacted with the polyester, water or methanol is eliminated. This modification improves the weatherability and/or heat resistance of the alkyd and resulting organic coating. The silicone-modified polyesters are available in both self-curing and baking (melamine formaldehyde resin cross-linked) types. They are used as coil coatings for prefabricated building panels, prefabricated architectural products, metal advertising sign stock, and other applications requiring excellent exterior durability and/or good heat resistance.

Higher Solids Types

Higher solids silicone-modified polyesters are made by lowering the polyester base molecular weight and/or using oxygenated solvents such as ketone and ester types as replacements for aromatic hydrocarbons. This substitution yields increased solvency, lower viscosities, lower solvent amounts, and higher nonvolatile content for the polyester solution. The end uses are similar to conventional solvent-borne silicone polyesters. However, the higher solids, silicone-modified polyester resins do not have the self-cross-link-

ing option available for conventional types and are always combined with a cross-linking agent.

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Amino Resins (Reaction Products of Melamine, Urea, etc. with Formaldehyde and Alcohols)

8

by J. Owen Santer[1]

INTRODUCTION

Definition and Description

AMINO, OR AMINOPLAST, RESINS for coatings are the products of the reaction of either urea (Fig. 1) or melamine (Fig. 2) with formaldehyde and an alcohol. Besides urea and melamine, other compounds with similar functionality—such as benzoguanamine, glycoluril, etc.—are also used in specific applications where certain property advantages are required. However, use of these materials is quite limited, and sales of amino resins are dominated by those based on urea and melamine, with U.S. consumption of about 100 million lb (45×10^6 kg) per year.

As prepared, amino resins are usually water-white, viscous materials which may contain added solvent to reduce viscosity for ease of handling. Where a solvent is used, it is most often an alcohol such as *n*-butanol, iso-butanol, or iso-propanol, all of which are excellent solvents for amino resins. Mixed solvents, such as *n*- or iso-butanol with xylene are also used, especially for the higher-molecular-weight resins made with butanol as a co-reactant. Some amino resins are water soluble or water reducible with co-solvent.

Amino resins for coatings are grouped somewhat arbitrarily into two classes: (1) high solids resins, i.e., resin solutions at ≥80% solids (weight/weight), including resins which contain no solvent, and (2) conventional resins, i.e., resin solutions at <80% solids (weight/weight).

History

Historically, the first amino resins used in coatings were the reaction products of urea or melamine with formaldehyde and butanol (either *n*- or iso-). They were substantially polymeric and were formulated at about 50 to 60% solids in butanol/xylene mixtures. They have been commercially available for about 60 years. Parenthetically, it should be noted that resins made by reacting urea or melamine with formaldehyde without subsequent reaction with an alcohol have been available for 70 years or more. These resins are used as molding powders and adhesives and are generally unsuitable for coatings applications.

High-solids coating resins, usually made with higher ratios of reacted formaldehyde than the older, conventional resins, have been available for about 35 years. They are almost always made with methanol or combinations of methanol and butanol, although a small number of high-solids resins are available which are made exclusively with butanol.

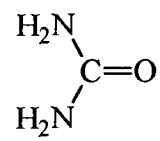

FIG. 1–Urea.

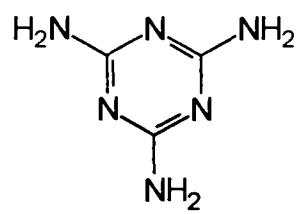

FIG. 2–Melamine.

Where Used

Amino resins are used in coatings to cross-link the primary film-former, usually an acrylic, polyester, or alkyd resin carrying primary or secondary hydroxyl groups. The cross-linking reaction ("cure") is principally one of trans-etherification between hydroxyl groups on the primary film-former and alkoxymethyl groups on the amino resin. In addition to the trans-etherification reaction, the amino resin almost always undergoes self-condensation reactions.

The major by-products of the cure reaction include methanol and/or butanol, formaldehyde, and water. Cure temperatures are in the range of 180 to 400°F (82 to 204°C) for times which vary from 20 to 30 min at the lower end of the temperature range to perhaps only 30 s at the upper end. An acid catalyst may be used to accelerate cure, depending on the cure temperature and the particular amino used. Claims have been made for amino resin formulations which cure at room temperature, but as far as is known, no such formulations are presently commercially available.

Urea resins are less expensive than melamine resins, which is understandable given that melamine is made from urea. Urea resins are also faster curing than melamine resins, but are moisture sensitive and therefore not suitable for use outdoors. They are used widely for wood finishing, e.g., furniture, kitchen cabinets, and in paper, film, and foil applica-

[1]Principal technologist, Monsanto Chemical Co., 730 Worcester Street, Springfield, MA 01151.

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tions. Wood and paper applications capitalize on the relatively rapid cure of the urea resin since lower temperatures must be used to avoid damage to the substrate. In some wood applications, cure temperature is at or near ambient.

Melamine resins, on the other hand, find much broader application since they are not nearly as water sensitive as the ureas. Perhaps the largest single use for melamine resins is in automotive OEM (original equipment manufacture), where the finished paint must stand up to extremes of temperature, humidity, and the degradative effects of sunlight, etc. Melamine resins are used also in coil coatings, metal containers, etc. (see **End Uses of Amino Resins**).

SYNTHESIS OF AMINO RESINS

Reactions of Synthesis

The synthesis of amino resins for coatings is a two-step process. In the first step, the parent compound is reacted with formaldehyde (methylolation reaction); in the second, the methylolated intermediate is reacted with an alcohol (etherification reaction). Equations 1 through 4 exemplify the process, with urea as the parent compound. Reactions with melamine are analogous.

$$H_2NCONH_2 + CH_2O \longrightarrow \underset{\text{monomethylolurea}}{H_2NCONHCH_2OH} \quad (1)$$

$$H_2NCONHCH_2OH + CH_2O \longrightarrow \underset{\text{dimethylolurea}}{HOCH_2NHCONHCH_2OH} \quad (2)$$

$$HOCH_2NHCONHCH_2OH + ROH \longrightarrow HOCH_2NHCONHCH_2OR + H_2O \quad (3)$$

$$HOCH_2NHCONHCH_2OR + ROH \longrightarrow \underset{\text{bis(alkoxymethyl)urea}}{ROCH_2NHCONHCH_2OR} + H_2O \quad (4)$$

Reactions shown in Eqs 1 and 2 proceed quite rapidly when catalyzed by either acid or base. Reactions shown in Eqs 3 and 4 take place only under acid conditions, with the rate of reaction strongly pH dependent; the lower the pH, the faster the reaction. All four reactions are equilibrium reactions. Hence, the extent of the reaction is dependent on the charge ratios of the various reactants and on whether or not the reactions are driven by removal of by-products in order to shift the equilibrium.

The reactions of melamine are similar to those of urea with one exception. With urea, two of the four available hydrogens are readily reacted with formaldehyde (Eqs 1 and 2), while the remaining two hydrogens react more slowly and require an excess of formaldehyde to force the reaction. With melamine, on the other hand, all six hydrogen atoms may be reacted with relative ease to give hexa(methylol)melamine.

The kinetics of the methylolation reactions of urea and melamine have been studied extensively [*1-7*], but there is nothing in the literature on the kinetics of the etherification reaction. Although both of these reactions are superficially straightforward, a number of other reactions may take place which complicate the kinetics. These reactions are all self-condensation reactions in which two or more molecules of the parent species are joined together through either a $>NCH_2N<$ (methylene) or $>NCH_2OCH_2N<$ (methylene ether) bridge. The reactions leading to self-condensation may be written as follows:

$$>NCH_2OR + HN< \longrightarrow >NCH_2N< + ROH \quad (5)$$
$$R = H, \text{alkyl}$$

$$>NCH_2OH + HOCH_2N< \longrightarrow >NCH_2OCH_2N< + H_2O \quad (6)$$

The bridging groups in amino resins manufactured for coatings applications are predominantly methylene ether bridges. When formulated and cured, additional bridges of both types may be formed; how many of each will depend on factors such as the composition of the amino resin, cure temperature, and catalyst level.

It can be seen, then, that a variety of amino resins may be prepared, with properties which depend on such factors as the choice of starting material, i.e., urea, melamine, etc., the combining ratios of the various reactants, the choice of alcohol (or alcohols, if more than one is used), and the degree of polymerization of the resin. The principal manufacturers of amino resins for coatings typically offer a product line of 25 or more resins. A generalized composition of a typical melamine resin is shown in Fig. 3.

Structure/Property Variations

The difference between conventional solids and high-solids amino resins represents not so much a difference in solids content as it does a distinction between resin structures. The conventional solids (<80%) resins are made from melamine or urea reacted with relatively low levels of formaldehyde, typically 1.5 to 2.0 mol for urea resins and 2.5 to 3.5 mol for melamine resins, and etherified with either *n*- or iso-butanol. Because of these low reaction ratios, considerable self-condensation takes place during the synthesis, leading in the case of melamine resins to products with degrees of polymerization (DP) ≥3 and perhaps somewhat higher for the ureas. Because of the relatively high polymer content, these resins are viscous and must be reduced with solvent to less than 80% to obtain a manageable viscosity.

Another, possibly the major, contributor to high viscosity is the residual imino (>NH) and methylol ($>NCH_2OH$) groups on the amino resin, which can form strong hydrogen bonds with unshared electrons on nitrogen and oxygen.

The high-solids amino resins have much higher levels of combined formaldehyde than the conventional solids resins. Typical values for combined formaldehyde are in the range 2.0 to 2.7 for urea resins and 3.5 to 6.0 for melamine resins. The etherifying alcohol is most often methanol, although res-

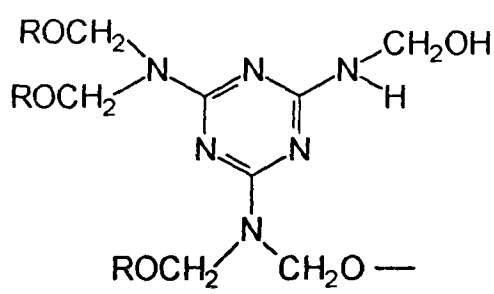

FIG. 3—Representative structure of a melamine resin.

ins made with both methanol and butanol or even butanol alone are also widely used. These resins are less polymeric, with DP <3, and usually more fully etherified and so less polar than the conventional resins. In some cases, these resins are sufficiently low in viscosity that no solvent is needed. Where solvent is required, it is usually either isopropanol or butanol (*n*- or iso-). Resins are also made which can be reduced with water.

Analysis/Analytical Methods

Structural analysis of amino resins has been reviewed by Christensen [*8*]. Methods discussed include ^{1}H NMR and ^{13}C NMR for determining levels of combined formaldehyde and alcohol, analysis of alkoxy groups by Zeisel cleavage, and by trans-etherification followed by gas chromatography. Christensen [*8*] and Kambanis and Rybicky [*9*] also describe nondestructive methods for removing solvent from amino resin solutions in order to determine nonvolatile content.

Classically, amino resins for coatings have been characterized by three test procedures. These procedures, which tell the coating formulator most of what he needs to know with regard to formulation and cure conditions, are measurement of (1) solids content, (2) viscosity, and (3) solvent tolerance. These are discussed below.

Solids Content

The most common methods used to determine solids content are gravimetric. Solvent is allowed to evaporate from a weighed sample under carefully controlled conditions of time and temperature. The sample is then reweighed. The loss in weight gives a measure of solvent content, and the solids content is obtained by difference. One difficulty with this test is the tendency of amino resins to deformylate and/or self-condense when heated, with evolution of formaldehyde, alcohol, and water. To the extent that this occurs, the measured solids content will be lower than the "true" value. Frequently, however, the paint formulator is interested in the "contributed solids," i.e., what fraction of the amino resin solution remains in the cured film. In that case, a solids test method which approximates the time and temperature of cure might be more appropriate.

For these reasons, solids test methods fall into two groups: (1) methods which reflect the solids content in the absence of self-condensation, etc., and (2) other methods, which reflect varying degrees of self-condensation in addition to loss of formaldehyde and solvent(s).

The most common of the first methods is the so-called foil solids test, which is used almost universally for high-solids amino resins. Essentially, a 1-g sample of resin solution is weighed onto a piece of preweighed aluminum foil. The foil is folded over on itself and the sample compressed between the two foil surfaces to provide a thin film about 3 to 4 in. (7 to 10 cm) in diameter. The foil is then opened up to give a thin film on each foil surface. The foil is placed in a 45°C oven for 45 min, at the end of which time it is removed, reweighed, and the solids content calculated. These conditions are known to be sufficiently mild that no resin condensation occurs; nor does the resin lose formaldehyde via demethylolation. Surprisingly, the foil solids test may on occasion overestimate the solids content, particularly when (1) the resin is relatively polar, i.e., carries appreciable >NH and $>NCH_2OH$ groups, and (2) the solvent is not low boiling. Apparently, the increase in viscosity as solvent evaporates slows the diffusion rate and effectively prevents complete removal of solvent within the time frame of the test. There may also be a hydrogen-bonding effect between solvent and resin which contributes to the retention of solvent.

Other test methods involve much higher temperatures, where resin condensation/degradation does occur. One standard method is the ASTM Test Methods for Volatile Content of Coatings (ASTM D 2369), where a small resin sample (0.3 to 0.5 g) is diluted with xylene and placed in a 110°C oven for 1 h. There are a number of other, similar tests.

Viscosity Measurement

Amino resin viscosities are most commonly measured by the Gardner bubble viscometer method. This method is similar to the Test Method for Viscosity of Transparent Liquids by Bubble Time Method (ASTM D 1545). A tube containing the resin under test is placed in a rack containing reference tubes of known viscosity. The tubes are equilibrated to 25°C in a constant temperature bath. The rack is quickly inverted, and the rate of rise of an air bubble in the sample tube is compared against similar bubbles in the reference tubes. The reference tubes are letter graded A through Z and Z1 through Z6.

Solvent Tolerance

There are a number of different solvent tolerance tests. All involve titrating a weighed sample of the amino resin with a standard reagent (solvent). The object of the test is to measure how much of the reagent the amino resin can accept before the solution turns cloudy/milky. Results are typically reported in milliliters of reagent per gram of sample. Typical reagents used include xylene, iso-octane, and the iso-octane/decahydronaphthalene/toluene mixture described in ASTM Test Method for Solvent Tolerance of Amine Resins (D 1198).

While the immediate objective of the solvent tolerance test is to determine the amount of reagent which the amino resin can accept before solution clouding occurs, the real purpose of the test is to gain insight into the structure and composition of the resin and hence have a better understanding of how it will perform in a given coating application. In general, amino resins of high molecular weight, or having high levels of polar functional groups, i.e., >NH, $>NCH_2OH$, will have limited compatibility with the typical hydrocarbons used and hence will give low tolerance test results. Experience shows that a low tolerance value means a faster curing resin and vice versa, especially in the absence of acid catalyst. However, although the tolerance test represents a quick and easy way to measure potential cure response, it does not uniquely define the resin structure. Thus, a low tolerance reading can be caused by either high polarity or high molecular weight or both.

Size Exclusion and High-Performance Liquid Chromatography

To obtain more detailed knowledge of resin structure, amino chemists now rely very heavily on gel permeation or size exclusion chromatography (SEC) and on high-performance liquid chromatography (HPLC). The size exclusion

chromatograph provides an excellent measure of number and weight-average molecular weight and molecular weight distribution (polydispersity), while HPLC, which fractionates the resin components primarily by functional groups, provides information on resin composition. The more polar species are eluted first, followed by the less polar fractions. Thus, taken together, SEC and HPLC provide detailed information on molecular weight and functionality which cannot be directly obtained or inferred from any of the various solvent tolerance tests. Size exclusion and liquid chromatograms for a representative commercial high-solids methylated melamine resin are shown in Figs. 4 and 5.

Combining Ratios

Amino resins may also be characterized by measurement of the amounts of formaldehyde and alcohol which have reacted. For example, see hexa(methoxymethyl)melamine (HMMM) (Fig. 6), which has exactly 6 mol each of combined formaldehyde and methanol per mole of melamine. Unlike HMMM, most resins are, of course, mixtures of products which are best described by an average composition. One of the most widely sold commercial high-solids methylated melamine resins has an average combining ratio melamine/formaldehyde/methanol of about 1/5.6/5.1. Because methanol reacts with an already-reacted formaldehyde molecule, a resin can never have combined methanol greater than the combined formaldehyde. The excess formaldehyde, 0.5 mol in the commercial example, represents formaldehyde which has not reacted with methanol and which must therefore be present as methylol ($>NCH_2OH$), bridging groups ($>NCH_2OCH_2N<$), and acetals ($>NCH_2OCH_2OCH_3$). Acetals are formed when an excess of formaldehyde is used in the

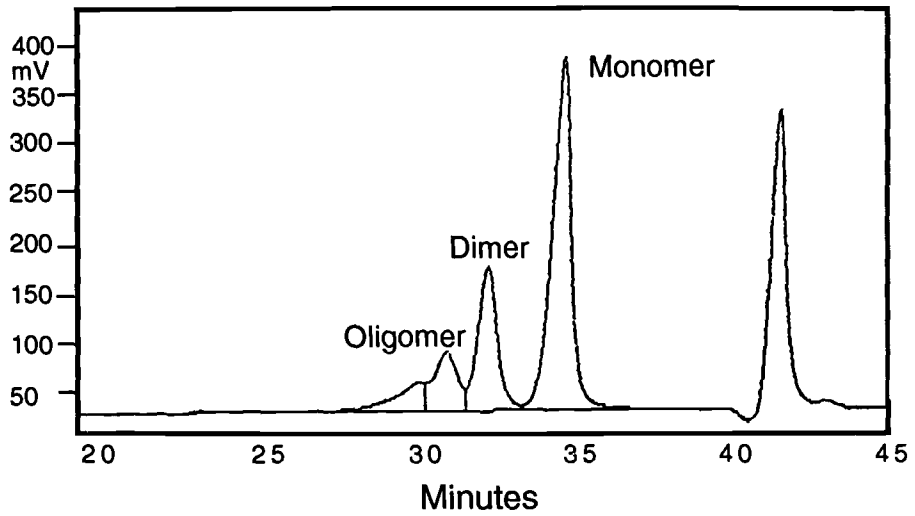

FIG. 4–Size exclusion chromatogram of a typical high-solids methylated melamine resin.

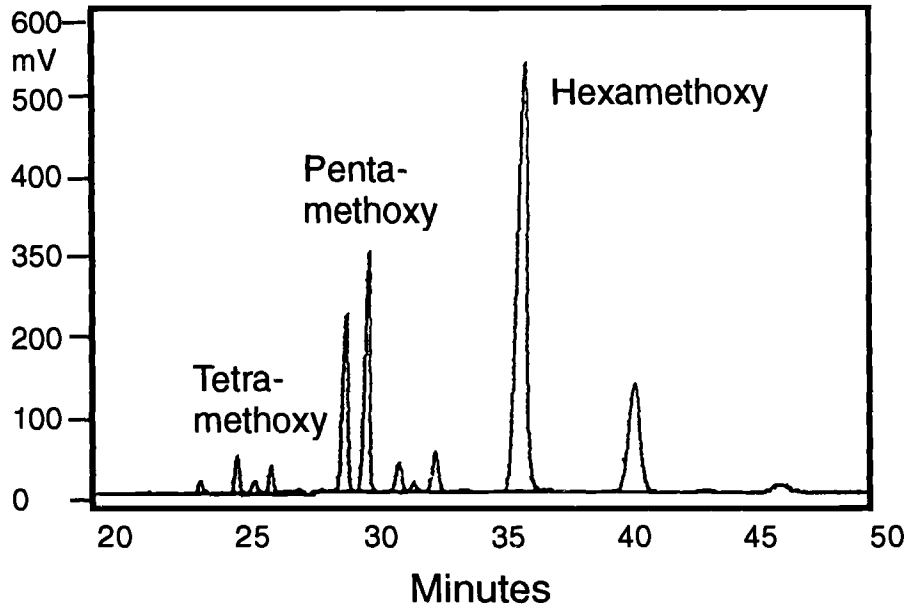

FIG. 5–High-performance liquid chromatogram of a typical high-solids methylated melamine resin.

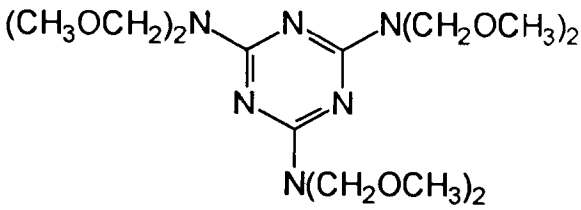

FIG. 6–Hexa(methoxymethyl)melamine.

synthesis. They are therefore present in many high-solids amino resins.

Determination of combining ratios may be done most easily by either ^{1}H or ^{13}C NMR techniques [8]. Older methods involve complete hydrolysis of the resin to the starting materials, followed by wet-chemical analysis for formaldehyde and gas chromatographic determination of alcohol (methanol or butanol).

Free Formaldehyde

Amino resins always contain some unreacted formaldehyde, usually referred to in product specifications as "free" formaldehyde. Free formaldehyde may be analyzed quantitatively by a number of methods. One of the most commonly used is the sodium sulfite method [10]. Formaldehyde reacts rapidly and completely with aqueous sodium sulfite to form a bisulfite addition complex. Sodium hydroxide is liberated quantitatively on a mole-for-mole basis

$$CH_2O + Na_2SO_3 + H_2O \longrightarrow NaOH + CH_2(OH)NaSO_3 \quad (7)$$

The NaOH is either titrated directly with a standard HCl solution, or neutralized with a known excess of standard HCl, which is then back-titrated with NaOH. Care must be taken to ensure that reacted formaldehyde, particularly methylol groups, is not analyzed as free formaldehyde. This can occur because of the following reaction, which can be minimized by performing the titration as rapidly as possible at cool temperatures, e.g., room temperature or lower.

$$>NCH_2OH \longrightarrow >NH + CH_2O \quad (8)$$

PHYSICAL PROPERTIES

General

Amino resins are typically viscous liquids, with an amine-like odor. Depending on composition, they may also smell of formaldehyde and/or solvent. They are readily soluble in alcohols, ketones, hydroxy-functional glycol ethers, esters, etc., but have limited solubility in hydrocarbons. Some resins, especially methylol-rich resins with low levels of both combined formaldehyde and combined methanol, are water soluble. Many more are water reducible in the presence of other solvents, e.g., alcohols and glycol ethers.

Because of their resinous nature, aminos have neither a well-defined freezing point nor boiling point. Uncured resins typically have glass transition temperatures around −40°C. When heated, they undergo decomposition, with release of formaldehyde and alcohol, at temperatures above about 140°C. This tendency to decompose causes difficulties in determining the solids content of resin solutions, as described in **Analysis/Analytical Methods**. The problem is particularly acute with resins having high methylol functionality.

Viscosity

The viscosity of an amino resin is a function of (1) polymer content (degree of polymerization) and (2) the nature of its functional groups. The latter may be a more important contributor to viscosity than the former.

Amino resins are not generally very polymeric, especially in comparison with other coating resins, e.g., polyesters, alkyds, and acrylics. Typically, average degrees of polymerization are in the range of 1 to 5. High-molecular-weight "tails" increase viscosity significantly.

Because of strong hydrogen bonding, resins carrying significant amounts of $>NH$ and $>NCH_2OH$ functionality are quite viscous, even though they may not be highly polymerized. There is a marked drop in viscosity when amino resins are diluted with solvent, largely due to breaking of hydrogen bonds. Good solvents (e.g., alcohols) are more effective at reducing viscosity than poor ones [11]. Methanol is probably the best, although it is not widely used because of its low boiling point. Isopropanol is almost as effective, and because it is somewhat higher boiling, represents a good compromise.

Surface Tension

The surface tension of amino resins is quite strongly related to the nature of the etherifying alcohol and is much less affected by the level of combined formaldehyde and alcohol. In the author's laboratory, surface tension measurements on high-solids, solvent-free resins using a DeNouy tensiometer have given values ranging from about 45 dynes/cm for methylated resins to about 28 dynes/cm for butylated resins. Mixed methyl/butyl resins give intermediate values, depending on the methyl and butyl content. The reduction in surface tension when butanol is the etherifying alcohol may be one reason that high-solids butyl and methyl/butyl resins provide improved flow and leveling in high-solids formulations compared to their fully methylated counterparts.

REACTIONS OF AMINOS IN COATINGS

Cure Reactions

Amino resins in coating formulations cure by reactions which are chemically and mechanistically similar to those which take place during synthesis of the resin. The principal reaction of cure is one of trans-etherification, wherein a hydroxyl group on the primary film-former (acrylic, polyester, or alkyd) reacts with an alkoxymethyl group on the amino resin

$$>NCH_2OR + HO{-}A \longrightarrow >NCH_2O{-}A + ROH \quad (9)$$

where

R = alkyl, and
A = primary film-former.

Additionally, direct etherification may take place, the end result being the same

$$>NCH_2OH + HO—A \longrightarrow >NCH_2O—A + H_2O \quad (10)$$

where

A = primary film-former.

These two reactions both result in chemical bond formation between the amino and the primary film-former (co-condensation). Two other reactions may also take place, both of which involve reaction of the amino resin with itself (self-condensation). These are

$$>NH + ROCH_2N< \longrightarrow >NCH_2N< + ROH \quad (11)$$

where

R = H, alkyl.

$$>NCH_2OH + HOCH_2N< \longrightarrow >NCH_2OCH_2N< + H_2O \quad (12)$$

Besides the co-condensation and self-condensation reactions, hydrolysis and deformylation reactions may also occur

$$>NCH_2OR + H_2O \longrightarrow >NCH_2OH + ROH \quad (13)$$

$$>NCH_2OCH_2OR + H_2O \longrightarrow >NCH_2OH + CH_2O + ROH \quad (14)$$

$$>NCH_2OH \longrightarrow >NH + CH_2O \quad (15)$$

The relative contributions to cure of the co-condensation and self-condensation reactions will depend on a variety of factors. These include:

1. The functionality of the amino resin, i.e., the relative proportions of $>NCH_2OR$, $>NCH_2OH$, and $>NH$ groups present initially, as well as those generated during formulation and/or cure.
2. The functionality (hydroxyl number) of the primary film-former (coreactant).
3. The amino/coreactant ratio.
4. The level and type of catalyst (weak acid/strong acid).
5. Cure time and temperature.

A coreactant resin with a low hydroxyl number is best if formulated with a "polar" amino (i.e., one rich in $>NH$ and/or $>NCH_2OH$) since these groups help build molecular weight during cure via self-condensation, particularly if little or no catalyst is present. Conversely, a high hydroxyl resin is best if matched with an alkoxymethyl-rich amino and cured with a strong acid catalyst. Where high cure temperatures are employed (e.g., can or coil coating operations), the choice of amino resin is less obvious, and, in practice, both polar and nonpolar aminos are used.

Acid catalysts are usually used as an aid in curing amino-based formulations. These catalysts include very strong acids such as *p*-toluenesulfonic acid (PTSA), dodecylbenzenesulfonic acid (DDBSA), dinonylnaphthalenedisulfonic acid (DNNDSA), etc., and weaker acids such as phenyl acid phosphate (PAP), butyl acid phosphate (BAP), etc. Amine blocking agents are sometimes used to help minimize resin advancement prior to cure. Some coatings, particularly those designed for high-bake temperatures, need no catalyst, relying instead on the combination of high temperature and perhaps carboxylic acid functionality on the primary film-former to bring about cure [*12*]. While all of the various reactions which take place during cure are accelerated by either acid or heat, it is fair to say that reactions of transetherification are most influenced by catalyst level and type, while reactions of self-condensation are most influenced by heat. The trans-etherification reaction takes place very rapidly under strong acid catalysis, even at low temperatures. This is especially true for aminos with a high level of alkoxymethyl substitution, i.e., a very low NH content, which tends to inhibit catalysis. Thus, most formulations involving resins with high alkoxymethyl ether content and designed for low-temperature cure (250°F or lower) will call for a sulfonic acid catalyst, either blocked or free.

Although the individual reactions of cure are reasonably well understood and have been described in numerous papers [*13-18*], there is still much to be learned about the overall behavior of amino resins during cure, in particular the relative contributions of each of the various reactions. One of the difficulties is, of course, that the coating becomes intractable as cure progresses. Hence, a majority of studies involve analysis of the by-products of cure [*13,17,30*]. Other methods, such as dynamic mechanical analysis [*19*], nuclear magnetic resonance [*20,21*], FTIR [*17*], ESCA, etc. investigate the structure of the cured film.

These techniques are useful not only for analyzing the freshly cured coating, but also as a means of following the coating through its lifetime, either natural or accelerated.

Degradation and Weathering

Amino-based cross-linked coatings exposed to the atmosphere are subject to both hydrolysis and UV-degradation.

The mechanisms by which melamine resins hydrolyze have been described in detail by Berge [*22–24*], who was the first to distinguish between mono- and di-substituted nitrogen with respect to their behavior towards acid or base hydrolysis. Thus, in an alkaline medium, hydrolysis of an alkoxymethyl group on a singly substituted nitrogen is initiated by removal by the base of the proton attached to nitrogen

$$—NHCH_2OR + B \longrightarrow —\tilde{N}CH_2OR + BH^+ \quad (16)$$

$$—\tilde{N}CH_2OR \longrightarrow —N = CH_2 + OR^- \quad (17)$$

$$—N = CH_2 + H_2O \longrightarrow —NHCH_2OH \quad (18)$$

$$OR^- + BH^+ \longrightarrow ROH + B \quad (19)$$

This mechanism is clearly not applicable to di-substituted nitrogen ($N(CH_2OR)_2$), and these groups are in fact extremely resistant to alkaline hydrolysis.

On the other hand, acid hydrolysis takes place readily for both mono- and di-substituted nitrogen. Berge proposed two mechanisms (a) specific acid catalysis

$$>NCH_2—OR + H^+ \longrightarrow >NCH_2OHR^+ \quad (20)$$

$$>NCH_2OHR^+ \longrightarrow >NCH_2^+ + ROH \quad (21)$$

$$>NCH_2^+ + H_2O \longrightarrow >NCH_2OH + H^+ \quad (22)$$

and (b) general acid catalysis

$$>NHCH_2OR + HA \longrightarrow >NCH_2OHR^+ + A^- \quad (23)$$

$$>NHCH_2OHR^+ + A^- \longrightarrow >N = CH_2 + ROH + HA \quad (24)$$

$$—N = CH_2 + H_2O \longrightarrow —NHCH_2OH \quad (25)$$

Berge's work with melamine resins is undoubtedly relevant to acid hydrolysis of paint films, which has been studied by a number of workers.

English et al. [*25,26*] found that coatings prepared from highly alkylated melamines underwent extensive hydrolysis of residual methoxy groups during two years exposure in Florida, but there was no evidence of hydrolysis of bonds between melamine and the primary film-former. Bauer [*27–28*] used IR to analyze acrylic-melamine coatings exposed to both UV and moisture and found evidence of hydrolysis of both residual methoxy groups and acrylic-melamine bonds, with the rate of hydrolysis being faster in the presence of UV light. The rate of hydrolysis was slowed considerably when a hindered amine light stabilizer was used.

In recent years, degradation of melamine-containing automotive coatings has been particularly severe because of etching and spotting due to "acid rain." The problem is compounded because modern high-solids automotive coatings use very high levels of melamine resins (35 to 45% of total binder weight), giving rise to correspondingly high levels of acrylic-melamine bonds and residual alkoxymethyl groups in the cured film, all of which are susceptible to hydrolysis under acid conditions. Suppliers of high-solids coatings for automobiles are presently evaluating and using alternative cross-linkers, such as isocyanates and epoxies, which are more stable under acid rain conditions and which can serve as either a partial or complete replacement for melamines. An interesting aspect of the acid etch problem is that the damage always occurs to relatively new coatings. If a newly painted automobile is protected from the acid environment for the first six to twelve weeks, damage thereafter is much less severe. An obvious conclusion is that the paint is undergoing additional cure (probably melamine self-condensation) as it ages.

Automotive paint manufacturers are also actively pursuing waterborne systems, which use higher molecular weight, less functional coreactant resins, and lower levels of melamine cross-linker and which are therefore less severely degraded by acid rain. At the present time, however, these waterborne systems are only used in the base coat, where acid attack is in any case minimized by the protective clear top coat. It is the top coat, with its high melamine content, which is the principal site for acid attack. But it is also the high level of melamine resin which provides the excellent gloss and "distinctness of image" (DOI), characteristic of basecoat/clearcoat technology. The melamine resin also minimizes the amount of solvent required because of its low viscosity at high-formulated solids, behaving in some ways as a reactive diluent and plasticizer.

End Uses of Amino Resins

Amino-based surface coatings protect and decorate the substrate to which they are applied. Their technology and use has developed over many years. As already mentioned, resins based on urea and melamine dominate the field. Urea resins are traditionally used in clear coatings for wood, e.g., furniture, kitchen cabinets, in paper, film, and foil applications, and in some appliance and general industrial coatings. They are also used to some extent in automotive primers. They cannot be used in automotive topcoats because of their sensitivity to hydrolysis.

Melamine resins are much more widely used. They give better chemical resistance, as well as resistance to weathering in exterior applications, despite some of the recent difficulties described earlier in connection with water spotting and acid etch of automobiles. Besides automobiles, they are used in appliance formulations (both coil appliance and conventional post-sprayed), general metal applications, container coatings (beer and beverage cans), etc.

In choosing an amino resin for a particular application, consideration must be given not only to interior versus exterior use, but also to possible restrictions on cure conditions and compatibility of the amino resin with its co-reactant resin, both when formulated and as the paint film is formed during solvent flash-off and cure, etc. Compatibility of the amino is especially important in water-borne coatings, which are becoming more widely used. Another factor is the stability of the amino towards advancement (molecular weight buildup) during storage of the formulated paint.

Benzoguanamine-based (Fig. 7) amino resins are used where film flexibility and hardness are required, as in some appliance applications (e.g., refrigerator doors made from coil stock, etc.). They also have good corrosion and humidity and detergent resistance. Their use is limited by cost and poor exterior durability due to the pendant phenyl group on the benzoguanamine molecule.

Glycoluril (Fig. 8) resins have been available for about a dozen years. They may require a higher cure temperature or a higher catalyst level than melamine-based resins, but show excellent corrosion and humidity resistance and release lower amounts of formaldehyde during cure [*29*].

ENVIRONMENTAL/TOXICITY

The past 20 years have seen increased emphasis on the quality of the environment both in the workplace and beyond. In the coatings industry, this has meant strict controls on exposure of workers to hazardous ingredients in the coating formulation when applied, as well as on the nature and

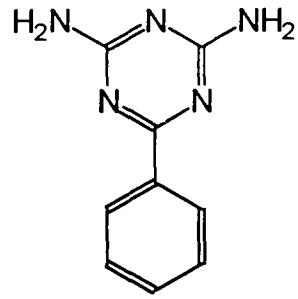

FIG. 7–Benzoguanamine.

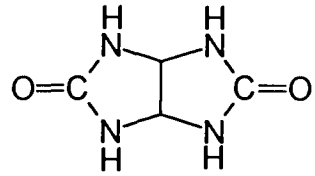

FIG. 8–Glycoluril.

amounts of volatile organics (the so-called VOCs) released to the environment when the formulation is cured.

Amino resin suppliers have responded to these environmental challenges in a number of ways. Chief among these has been a progressive shift towards higher-solids, lower-molecular-weight aminos, which are now the resins of choice of coatings formulators. Many amino resins are supplied at 100% nonvolatiles, especially for the automotive industry. Where solvents are needed, those presenting the least hazard to worker and environment are selected. For their part, paint producers have increased the functionality of the coreactant resin while lowering its molecular weight to minimize solvent use with the object of building molecular weight to the maximum possible extent during cure. This has meant using higher levels of amino resin, as much as 40 to 50% of total binder weight in some cases.

Perhaps the most intractable environmental problem with amino resins is the use of formaldehyde in their manufacture. Formaldehyde is recognized by the International Agency for Research on Cancer (IARC) as a carcinogen. The American Conference of Governmental Industrial Hygienists (ACGIH) lists formaldehyde as an "A2" substance, i.e., one suspected of carcinogenic potential for man, and the Occupational Safety and Health Administration (OSHA) has set workplace exposure limits of 0.75 ppm (8-h time weighted average) and 2 ppm (15-min short-term exposure limit).

The formaldehyde content of amino resins is predominantly "combined," i.e., chemically reacted, and represents about 30 to 50% by weight of the resin. A small amount, ranging from about 0.1 to about 3% is present free, or unreacted (see the section entitled **Analysis/Analytical Methods**). Amino resin suppliers have made considerable progress over the past several years in lowering the level of free formaldehyde in their products, which is important because of OSHA labelling requirements.

In an ideal situation, all of the combined formaldehyde would remain in the coating after cure as part of the polymer network. In practice, however, some of the combined formaldehyde and all of the free formaldehyde is released during cure and may reach the environment, depending on the mechanics of the coating and curing operation. It is the partial release of combined formaldehyde during cure which is of most concern, since the amount released can easily be several times that of the free formaldehyde. Incineration of off gases, where possible, is the best solution.

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9

Ceramic Coatings

by Richard A. Eppler[1]

CERAMIC COATINGS ARE AN ALTERNATIVE to organic paints for surface coating applications. When painting with a suitable material will meet all service requirements, it is almost always less expensive to paint. However, organic paints have limitations in several areas where ceramic coatings are a more suitable selection.

Vitreous (glassy) ceramic coatings are chosen for application over a substrate for one or more of several reasons [*1*]. These coatings may be applied to a substrate surface in preference to an organic paint to render the surface chemically more inert, impervious to liquids and gases, more readily cleanable, and more resistant to service temperature, abrasion, and scratching.

The chemical durability of ceramic coatings in service substantially exceeds that of organic paints [*2*]. Vitreous coatings are formulated to be resistant to a variety of reagents, from acids to hot water to alkalies, as well as to essentially all organic media. The only important exception is hydrofluoric acid, which readily attacks all silicate glasses. This outstanding durability, combined with a very smooth surface, renders many ceramic coatings suitable for applications requiring the highest standards of cleanability such as ware that comes in contact with food and drink. These coatings are also suitable for applications requiring true hermeticity, usually to protect sensitive electronic equipment. No organic resins are truly hermetic.

Even the most thermally stable organic resins depolymerize at temperatures on the order of 300°C. Hence, organic paints are not suitable for applications requiring thermal stability above 300°C. For example, stove side panels are painted, but stove tops are porcelain enameled. A similar argument can be made for abrasion resistance. Organic resins are soft (Moh 2 to 3). By contrast, vitreous coatings are harder (Moh 5 to 6), and some plasma coatings are much harder. For example, alumina coatings, plasma sprayed, have Moh = 9.

Vitreous coatings are thin layers of glass fused onto the surface of the substrate. When the substrate is a ceramic, the coating is called a glaze. When the substrate is a metal, the coating is called a porcelain enamel. When the substrate is a glass, the coating is called a glass enamel.

[1]Consultant, Eppler Associates, 400 Cedar Lane, Cheshire, CT 06410.

GLAZES

A ceramic glaze is a vitreous coating applied to a ceramic substrate, usually a whiteware. Glazes are applied to their substrates by one of several powder-processing techniques: dipping, spraying, and waterfall. The raw materials are both crystalline oxides and frits. In these wet processes the raw materials are dispersed in an aqueous slip for application. After application, the coatings must be dried and fired at high temperatures (up to 1300°C, typically 1000 to 1100°C) to fuse them onto the substrate.

Applications for Glazes

Ceramic glazes find their way into a wide range of applications ranging from coffee mugs to automotive spark plugs. The major markets for ceramic coatings have different requirements, but one common theme is chemical durability and cleanability.

The major products that normally use glazes are distributed as follows:

43.9%	Sanitaryware
32.9%	Wall and floor tile
10.9%	Tableware
9.5%	Artware
2.8%	Electrical porcelain and electronics

The total market for these products in the United States was reported to be $3459 billion for 1989 [*3*], of which the glaze typically consumed 10 to 15% of the total manufacturing cost. Hence, the value of the protective, functional, and decorative properties provided by the coating usually far outweighs the cost.

Leadless Glazes

Glazes are essentially mixtures of silica with other oxides added to permit the glaze to form at a readily achievable temperature. In a leadless glaze, the alkali and alkaline earth oxides, together with magnesia (MgO), zinc oxide (ZnO), and boron oxide (B_2O_3), are used to provide the fluxing action. Table 1 gives the formulas of a few typical ceramic glazes. Glaze 1 is a feldspathic glaze suitable for use on soft paste porcelains or hard stoneware [*4*]. This glaze is typical of that used on medieval Chinese porcelains.

Glaze 2 is a sanitary-ware glaze [*5*]. It is derived from the soft paste porcelain glaze by the addition of ZnO in large quantity. Increasing the melting rate by increasing the per-

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TABLE 1—Typical ceramic glazes in weight percent.

Glaze	Na_2O	K_2O	CaO	MgO	ZnO	SrO	BaO	PbO	B_2O_3	Al_2O_3	SiO_2	ZrO_2
1	2.24	3.24	9.71	0.44	0.00	0.00	0.00	0.00	0.00	14.44	69.90	0.00
2	2.05	3.12	11.15	0.00	5.39	0.00	0.00	0.00	0.00	18.58	59.71	0.00
3	6.54	1.47	7.67	0.16	10.18	0.00	0.00	0.00	1.36	10.36	62.25	0.00
4	1.81	2.71	9.16	0.62	10.94	3.07	2.50	0.00	5.47	7.37	55.79	0.57
5	3.06	1.72	7.65	0.00	0.00	0.00	0.00	16.08	6.04	9.57	55.88	0.00
6	2.46	0.00	3.09	0.00	0.00	0.00	0.00	35.30	8.93	7.04	42.45	0.72
7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	88.14	0.00	0.00	11.86	0.00
8	0.85	1.91	10.08	0.00	0.00	0.00	0.00	28.87	4.20	9.17	35.99	8.92

cent of fluxes yields a fast-fire, wall-tile glaze such as Glaze 3 [*6*]. To produce a glaze for dinnerware, the coefficient of thermal expansion must be reduced to match that of the ware. Glaze 4 is an example of a glaze for vitreous hotel china [*7*].

Lead-Containing Glazes

Litharge (PbO) is used in glazes for several reasons [*8*], the most important of which is the strong fluxing action of PbO, which allows the formulation of glazes that mature at temperatures lower than their leadless counterparts, leading to greater flexibility in the formulation of the glaze to obtain desired properties. Glazes for electronic substrates, artware, and some dinnerware, and tiles contain lead oxide. However, PbO is highly toxic. Therefore, use of lead-containing glazes requires special care in processing and in testing the ware produced.

Glaze 5 in Table 1 is an example of a lead-containing dinnerware glaze [*9*]. Glaze 6 is an example of a clear glaze suitable for use on artware and hobbyware bodies [*10*]. Glaze 7 is an example of a coating used on integrated circuit packages to seal them [*11*].

Satin and Matte Glazes

Satin and matte effects are due to dispersed oxide crystals of appropriate refractive index in the glaze [*5*]. Calcium aluminosilicate and zinc silicate crystals are commonly used. The crystals must be very small and evenly dispersed if the glaze is to have a smooth, velvet appearance. Glaze 8 in Table 1 is an example of a matte glaze.

Testing of Glazes

ASTM Committee C-21 on Ceramic Whitewares and Related Products has developed several test methods to evaluate the physical properties of ceramic glazes. These are listed in Table 2 [*12*]. These tests form the basis for most quality control testing programs.

There are several methods concerned with the fit of the glaze to the substrate. These include: C 554—Test Method for Crazing Resistance of Fired Glazed Ceramic Whitewares by a Thermal Shock Method; C 424—Test Method for Crazing Resistance of Fired Glazed Whitewares by Autoclave Treatment; C 539—Test Method for Linear Thermal Expansion of Porcelain Enamel and Glaze Frits and Ceramic Whiteware Materials by the Interferometric Method; and C 372—Test Method for Linear Thermal Expansion of Porcelain Enamel and Glaze Frits and Fired Ceramic Whiteware Products by the Dilatometer Method.

TABLE 2—Test methods for ceramic glazes [*12*].

Number	Title
C 1027	Test Method for Determining Visible Abrasion Resistance of Glazed Ceramic Tile
C 650	Test Method for Resistance of Ceramic Tile to Chemical Substance
C 609	Test Method for Measurement of Small Color Differences Between Ceramic Wall or Floor Tile
C 554	Test Method for Crazing Resistance of Fired Glazed Ceramic Whitewares by a Thermal Shock Method
C 424	Test Method for Crazing Resistance of Fired Glazed Whitewares by Autoclave Treatment
C 556	Test Method for Resistance of Overglaze Decorations to Attack by Detergents
C 539	Test Method for Linear Thermal Expansion of Porcelain Enamel and Glaze Frits and Ceramic Whiteware Materials by the Interferometric Method
C 372	Test Method for Linear Thermal Expansion of Porcelain Enamel and Glaze Frits and Fired Ceramic Whiteware Products by the Dilatometer Method
C 584	Test Method for 60-deg Specular Gloss of Glazed Ceramic Whitewares and Related Products
C 1034	Test Method for Lead and Cadmium Extracted from Glazed Ceramic Cookware
C 738	Test Method for Lead and Cadmium Extracted from Glazed Ceramic Surfaces
C 895	Test Method for Lead and Cadmium Extracted from Glazed Ceramic Tile

Several other ASTM methods are concerned with chemical durability. These include: C 650—Test Method for Resistance of Ceramic Tile to Chemical Substances; and C 556—Test Method for Resistance of Overglaze Decorations to Attack by Detergents. Of particular concern are ASTM methods used to control release of lead and cadmium from glazed surfaces. These include: C 1034—Test Method for Lead and Cadmium Extracted from Glazed Ceramic Cookware; C 738—Test Method for Lead and Cadmium Extracted from Glazed Ceramic Surfaces; and C 895—Test Method for Lead and Cadmium Extracted from Glazed Ceramic Tile; as well as C 1035—Specification for Lead and Cadmium Extracted from Glazed Ceramic Cookware.

PORCELAIN ENAMELS

Porcelain enamel coatings are ceramic coatings designed for application to metals. Conventional porcelain enamel coatings are prepared in an aqueous system and applied to the substrate by spray, dip, or flow coating. The coating is

dried before firing. Newer technology involves dry application of powdered porcelain enamel by electrostatic spray.

The total market for porcelain-enameled products was reported to be $5486 billion in 1989 [*13*]. About 86% of the products are appliances, such as ranges, water heaters, home laundry, and dishwashers. About 6% are cast-iron sanitary ware, and 8% are architectural, cookware, and miscellaneous items.

A porcelain enamel must be formulated such that it will bond to the metal substrate. For proper adherance of the enamel to the metal, it is necessary to develop a continuous electronic structure across the interface [*14*]. This structure is developed by saturating the enamel coating and the substrate metal with an oxide of the metal [*15*], which for iron and steel substrates is ferrous oxide (FeO).

Certain transition metal oxides, such as cobalt oxide (CoO), nickel oxide (NiO), and cupric oxide (CuO), can be added to an enamel formulation to improve the adherence between the metal and the substrate. Ground coat enamels contain adherance oxides, while cover coat enamels do not.

Ground Coat Enamels

A general-purpose ground coat enamel like Enamel 1 in Table 3 is an alkali borosilicate containing small amounts of adherance oxides to promote the bonding process. Enamel 2 is a home laundry enamel that has been formulated for outstanding alkali resistance through the addition of large quantities of zirconia (ZrO_2) [*16*]. Hot water tank coatings like Enamel 3 have very stringent thermal- and corrosion-resistance requirements.

Enamel 4 is a continuous clean coating. This is a porous coating which provides a means of volatilizing and removing food soils from the internal surfaces of ovens during normal operation [*17*].

Cover Coat Enamels

Cover coat porcelain enamels are formulated to provide specific color and appearance characteristics, abrasion resistance, surface hardness, and resistance to corrosion, heat, and thermal shock. They can be clear, semiopaque, or opaque. Opaque enamels such as Enamel 5 are used for white and pastel coatings [*18*]. They contain high concentrations of titania (TiO_2) to provide the opacification. Semiopaque enamels like Enamel 6 are used for most medium-strength colors. Clear enamels like Enamel 7 are used to produce strong, bright colors. They are similar to ground coat formulations without the adherance oxides.

Testing of Porcelain Enamels

Test methods for porcelain enamel coatings are under the jurisdiction of ASTM Committee B-8 on Metallic and Inorganic Coatings. The methods are listed in Table 4. Again, they form the basis for most quality control test programs.

Several of these test methods are concerned with the chemical durability of porcelain enamels. They include: C 282—Test Method for Acid Resistance of Porcelain Enamels (Citric Acid Spot Test); C 614—Test Method for Alkali Resistance of Porcelain Enamels; C 756—Test Method for Cleanability of Surface Finishes; C 538—Test Method for Color Retention of Red, Orange, and Yellow Porcelain Enamels; C 872—Test Method for Lead and Cadmium Release from Porcelain Enamel Surfaces; and C 283—Test Method for Resistance of Porcelain Enameled Utensils to Boiling Acid. A related issue is the possibility of defects providing a pathway from the surface to the substrate, usually called continuity of coating. Methods in this area include: C 536—Test Method for Continuity of Coatings in Glassed Steel Equipment by Electrical Testing; C 743—Test Method for Continuity of Porcelain

TABLE 3—Typical porcelain enamels in weight percent.

Oxide	Enamel 1	Enamel 2	Enamel 3	Enamel 4	Enamel 5	Enamel 6	Enamel 7
Li_2O	0.88	0.81	1.33	0.52	0.89	1.10	1.76
Na_2O	13.15	12.60	13.92	7.30	9.41	8.58	12.23
K_2O	2.30	1.56	0.00	1.47	6.13	9.15	3.83
CaO	6.18	2.80	2.04	0.65	0.00	0.00	0.00
MgO	0.00	0.18	0.00	0.00	0.00	0.00	0.00
ZnO	0.00	0.26	1.27	0.00	0.00	1.04	0.00
BaO	7.27	0.73	0.56	0.00	0.00	0.00	0.00
CoO	0.47	0.36	0.47	0.03	0.00	0.00	0.00
NiO	0.29	0.31	0.00	0.03	0.00	0.00	0.00
CuO	0.20	0.00	0.00	13.99	0.00	0.00	0.00
B_2O_3	15.37	15.99	7.60	1.18	16.13	16.53	7.11
Al_2O_3	6.35	11.50	2.02	41.38	2.25	1.34	2.72
Cr_2O_3	0.00	0.00	0.00	1.24	0.00	0.00	0.00
Sb_2O_3	0.00	0.00	0.00	0.30	0.00	0.00	0.00
SiO_2	44.01	41.55	56.05	24.20	40.97	46.74	59.07
ZrO_2	0.00	6.36	11.66	7.24	0.00	0.00	7.86
TiO_2	0.00	2.55	0.00	0.03	20.97	13.25	3.58
MnO_2	0.20	0.66	1.81	0.03	0.00	0.00	0.00
P_2O_5	0.70	0.45	0.00	0.00	1.30	0.00	0.00
Nb_2O_5	0.00	0.00	0.00	0.00	0.06	0.00	0.00
WO_3	0.00	0.00	0.00	0.00	0.05	0.00	0.00
MoO_3	0.00	0.00	0.00	0.00	0.00	0.00	0.47
F	2.71	2.31	2.19	0.72	3.17	3.93	2.35

Enamel Coatings; and C 537—Test Method for Reliability of Glass Coatings on Glassed Steel Reaction Equipment by High Voltage.

GLASS ENAMELS

Glass enamels are vitreous coatings applied on glass. They provide a means of decoration, not an improvement in chemical durability or in cleanability. These coatings must be matured at temperatures below the deformation point of glass (1000 to 1200°F or 538 to 649°C). Hence, they require large quantities of fluxing elements so that chemical durability is difficult to achieve.

Glass enamels are produced in ready-to-use form (paste, thermoplastics, spray mediums, ultraviolet curable mediums) by a few select manufacturers. They represent a specialty product that is more akin to organic paints than to other ceramic coatings. The markets for this specialty product are categorized as tableware, glass containers, architectural, lighting, and automotive. As supplied to the user, glass enamels are mechanical mixtures of pigments, fluxes, and organic suspending media. The requirement for low maturing temperatures necessitates the use of very high lead oxide containing borosilicates for the flux. Leadless fluxes are under development, but have not yet achieved commercially acceptable properties. The organic suspending media are similar to materials used to make organic paints.

TABLE 4—Test methods for porcelain enamels [*19*].

Number	Title
C 448	Test Methods for Abrasion Resistance of Porcelain Enamels
C 282	Test Method for Acid Resistance of Porcelain Enamels (Citric Acid Spot Test)
C 614	Test Method for Alkali Resistance of Porcelain Enamels
C 756	Test Method for Cleanability of Surface Finishes
C 538	Test Method for Color Retention of Red, Orange, and Yellow Porcelain Enamels
C 839	Test Method for Compressive Stress of Porcelain Enamels by Loaded-Beam Method
C 536	Test Method for Continuity of Coatings in Glassed Steel Equipment by Electrical Testing
C 743	Test Method for Continuity of Porcelain Enamel Coatings
C 374	Test Methods for Fusion Flow of Porcelain Enamel Frits (Flow-Button Methods)
C 346	Test Method for 45-degree Specular Gloss of Ceramic Materials
C 872	Test Method for Lead and Cadmium Release from Porcelain Enamel Surfaces
C 539	Test Method for Linear Thermal Expansion of Porcelain Enamel and Glaze Frits and Ceramic Whiteware Materials by the Interferometric Method
C 537	Test Method for Reliability of Glass Coatings on Glassed Steel Reaction Equipment by High Voltage
C 283	Test Method for Resistance of Porcelain Enameled Utensils to Boiling Acid
C 285	Test Method for Sieve Analysis of Wet-Milled and Dry-Milled Porcelain Enamel
C 703	Test Methods for Spalling Resistance of Porcelain-Enameled Aluminum
C 385	Test Method for Thermal Shock Resistance of Porcelain-Enameled Utensils

TABLE 5—Test methods for glass enamels [*12*].

ASTM Method	Subject
C 724	Test Methods for Acid Resistance of Ceramic Decorations on Architectural-Type Glass
C 735	Test Method for Acid Resistance of Ceramic Decorations on Returnable Beer and Beverage Glass Containers
C 675	Test Methods for Alkali Resistance of Ceramic Decorations on Returnable Beverage Glass Containers
C 676	Test Method for Detergent Resistance of Ceramic Decorations on Glass Tableware
C 824	Practice for Specimen Preparation for Determination of Linear Thermal Expansion of Vitreous Glass Enamels and Glass Color Frits by the Dilatometer Method
C 927	Test Method for Lead and Cadmium Extracted from the Lip and Rim Area of Glass Tumblers Externally Decorated with Ceramic Glass Enamels
C 978	Test Method for Photoelastic Determination of Residual Stress in a Transparent Glass Matrix Using a Polarizing Microscope and Optical Retardation Compensation Procedures
C 777	Test Method for Sulfide Resistance of Ceramic Decorations on Glass

Testing of Glass Enamels

Test methods for glass enamels are under the jurisdiction of Subcommittee 14.10 on Glass Decoration of ASTM Committee C-14 on Glass and Glass Products. These methods [*12*] are listed in Table 5.

Most of these methods are concerned with the chemical durability of glass decorations. They include: C 724—Test Methods for Acid Resistance of Ceramic Decorations on Architectural-Type Glass; C 735—Test Method for Acid Resistance of Ceramic Decorations on Returnable Beer and Beverage Glass Containers; C 675—Test Methods for Alkali Resistance of Ceramic Decorations on Returnable Beverage Glass Containers; C 676—Test Method for Detergent Resistance of Ceramic Decorations on Glass Tableware; and C 927—Test Method for Lead and Cadmium Extracted from the Lip and Rim Area of Glass Tumblers Externally Decorated with Ceramic Glass Enamels.

REFRACTORY COATINGS

Flame spray techniques can be used to apply ceramic coatings in the molten state to heat-sensitive or massive substrates that cannot themselves be heated to high temperatures. Most ceramic coating materials used currently can be applied by flame spraying [*20*]. Silicates, silicides, carbides, oxides, and nitrides have all been deposited by this process.

In these processes, the coating material is melted and projected as heated particles onto the substrate, where it instantaneously solidifies as a coating. Three methods of heating and propelling the particles in a plastic condition to the substrate surface include: (1) combustion flame spraying, (2) plasma arc flame spraying, and (3) detonation gun spraying. Combustion flame spraying is used for coating materials that melt readily. Plasma arc flame spraying is used for very re-

fractory materials such as metal carbides. Detonation gun spraying is used for hard, wear-resistant materials such as tungsten carbide.

Flame spray coatings generally lack smoothness and are usually porous. They are, therefore, limited to applications such as thermal barrier coatings, where porosity is a virtue, and wear-resistant coatings, where the materials cannot be applied readily by any other technique.

Testing of Refractory Coatings

There is only one test method for flame spray coatings in the ASTM standards: C 633—Test Method for Adhesion or Cohesive Strength of Flame-Sprayed Coatings [*19*].

COATING APPLICATION

Ceramic coatings are applied to their substrates by one of several powder-processing techniques. In wet processes the raw materials are dispersed in a slip. Slip preparation involves mixing the ingredients, particle-size reduction, dispersion in water, and the addition of minor amounts of additives to modify the rheological properties of the slip [*21–22*]. These processes are carried out together in a ball mill comprising a rotating cylinder partly filled with freely moving, impact-resistant shapes.

The application process for a ceramic coating must be straightforward and foolproof, reproducible, economical, and flexible [*21*]. Selection of the application technique is one of the most important decisions the coatings engineer makes. Criteria for this selection are type of ware, shape and size of ware, throughput required, energy and labor costs, and space available. All of these factors affect the quality and the cost of a coating process, so that the best solution must be determined on an individual basis.

Dipping is a simple, efficient, rapid technique requiring no capital equipment. The ware is immersed in the coating slip, moved around in a controlled way, removed from the slip, shaken to remove excess slip, and set down to drain and dry. Any bare spots are touched up with a finger wet with coating material. Its limitations are extreme sensitivity to operator skill and difficulty in automating volume production.

Spraying is a process whereby a coating slip is broken down into a cloud of fine particles that are transferred to the substrate by either pneumatic, mechanical, or electrical forces. The method requires a gun, a container or feed mechanism, an impelling agency, and a properly designed hood or booth maintained under negative pressure [*23*]. Spraying lends itself to high-volume automated systems [*24*]. The articles are continuously fed under a battery of angled spray guns. Coating reclaim is an essential part of automated systems.

Slip can also be applied mechanically with a rotating atomizer. Slip is passed onto a set of closely spaced rotating disks which throw the coating into a fan of droplets. Costs are similar to spraying. The primary use of this technique is in producing textured coatings on tile.

If the substrate is conductive (that is, a metal), the surface quality and uniformity of a ceramic coating can be improved by using the electrostatic spray coating technique [*25,26*]. In this system, the slip is broken into droplets either by air atomization or by centrifugal force from a sharp-edged rotating surface. The drops acquire a high negative charge and are dispersed as a fine mist. They are driven forward to the grounded substrate following the lines of force. Hence, coating material can reach the underside of the ware, and full-edge coverage is achieved.

There are other techniques for specific applications. Tile require only one face to be glazed, but with a very smooth coating. This suggests the waterfall, or curtain technique [*21*], where a continuous feed of tiles is carried under a curtain of fluid slip. Painting and brushing are seldom used except for special effects and for applying glaze to inaccessible areas.

For substrates which require precisely positioned areas of coating, the silk screen process can be used [*20*]. Finely powdered dry coating material is dispersed as a smooth paste. Using a squeegee, this paste is pressed through the open areas of a fine mesh screen stretched on a frame. For coating a total piece, costs are excessive.

There are a few techniques of application that do not require the preparation of a slip. They include flame spraying, dry powder cast iron enameling, and electrostatic dry powder enameling.

Flame spraying can be used to apply ceramic coatings in the molten state to heat-sensitive or massive substrates. Flame spray coatings generally lack smoothness and are usually porous. Equipment and material costs are generally high.

In dry powder cast-iron enameling, a casting is heated in a furnace to red heat. It is then withdrawn from the furnace and, while still hot, dusted with dry powdered frit by means of a vibrating sieve placed over the surfaces to be coated. The powdered frit melts and adheres as it falls on the hot surface. This process is also extremely operator sensitive.

The most important dry application method, and the one most recently introduced, is dry powder electrostatic application of all-fritted coatings to conductive substrates. This technique involves charging individual coating particles at a high voltage and then spraying them towards the substrate surface. Charging of particles is accomplished by encapsulating the coating material with an organic silane. It is then suspended in clean compressed air in a fluidized bed container [*27*]. The fluidized powder is siphoned and propelled through powder feed tubes to special electrostatic powder guns for low-pressure application. The powder carries a potential of up to 100 kV, which causes it to seek out and attach itself to the grounded workpiece. Capital costs of this process are substantial, but operating costs are reduced through elimination of slurry preparation and drying of the ware.

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10

Epoxy Resins in Coatings

by Ronald S. Bauer,[1] Edward J. Marx,[2] and Michael J. Watkins[2]

EPOXY RESINS HAVE BECOME technologically important materials that find extensive application in high-performance coatings, adhesives, and reinforced plastics. Almost since their commercial introduction in 1950, epoxy resin systems have been used in protective coatings. Historically, protective coatings were the largest single end use for epoxy resins. Although in recent years the noncoating applications of epoxy resin have been growing, coatings still represent about half of the annual epoxy resin usage.

Epoxy resin coatings offer a unique combination of adhesion, chemical resistance, and physical properties that provide outstanding protection against severe corrosive environments. They are used extensively in coatings for refineries, chemical plants, and marine equipment such as offshore drilling platforms and merchant ships. Other important applications where epoxy resin coatings are used almost exclusively because of the corrosion protection they afford include automotive, aircraft, and appliance primers as well as to protect both the inside and outside of pipe. Epoxy resins are the predominant thermosetting resin used for the interior linings of beer and beverage cans, cans for hard-to-contain food products such as sauerkraut, tomato juice, and meat products, and for chemical-resistant linings of pails and drums. These coatings are used not only to protect the metal of the container from corrosion, but also to protect the flavor of the contents, which can be affected by direct contact with metal.

The principal components of any epoxy resin coating system are the epoxy resin and the curing agent or hardener. Epoxy resins are reactive intermediates that can be liquid or solid, and they are converted into the final coating by reaction with curing agents (hardeners). Curing agents function by reacting with specific groups in the epoxy resin molecule to give a three-dimensional, infusible polymer network. Although the resin and curing agent are common to all epoxy coatings, other materials are incorporated to achieve the desired rheological characteristics, cure speed, and film performance.

RESIN TYPES

Generically, epoxy resins can be characterized as a group of commercially available oligomeric materials which contain one or more epoxy (oxirane) groups per molecule. The epoxy resins most widely used by far in coatings are the bisphenol A based epoxy resins, the generalized structure of which is given in Fig. 1. In commercial products, the n value ranges from 0 to about 25, although higher-molecular-weight thermoplastic resins having n values of 200 or more are available. As n increases, the epoxy equivalent weight (EEW) increases, as does the number of hydroxyl groups. Thus epoxy resins with low n values are normally cured by reaction of the epoxy group, whereas those resins with higher n values are cured by reaction of the hydroxyl functionality.

Resins having n values less than 1 are viscous liquids; they are used mainly in ambient-temperature cure coatings, electrical castings, flooring, electrical laminates, and fiber-reinforced composites. These applications require liquid resins having good flow and are cured through the epoxy ring. The higher n value resins, particularly those above 3000 molecular weight, are normally used in solution and find their greatest application in heat-cured coatings. In these resins the concentration of epoxy groups is low, and so they are cured with materials that react with the hydroxyl groups along the backbone. Table 1 displays a range of typical epoxy resins that are commercially available along with their properties and applications.

CURING AGENTS

Epoxy resins are reactive intermediates composed of mixtures of oligomeric materials containing one or more epoxy groups per molecule. To convert epoxy resins into useful products, they must be cross-linked or "cured" into a three-dimensional polymer network. Cross-linking agents, or curing agents as they are generally called, function by reaction with or cause the reaction of epoxide or hydroxyl groups in the epoxy resin. The number of curing agents that have been developed over the years for epoxy resins is overwhelming. Selection of the curing agent is as important as that of the base resin; it is dependent on the performance requirements of the film and the constraints dictated by the specific method of application.

The most important types of curing agents used in epoxy resin coatings are the amine-functional materials for ambient-cure coatings and the amino- and phenoplast resins for heat-cured systems. The principal amine-functional curing agents used in ambient-cure coatings are aliphatic amine adducts of epoxy resins, polyamides, and ketimines. Amine-functional materials cure epoxy resins by polyaddition

[1]Research adviser and [2]senior research chemist, Shell Development Co., Westhollow Research Center, P.O. Box 1380, Houston, TX 77521-1380.

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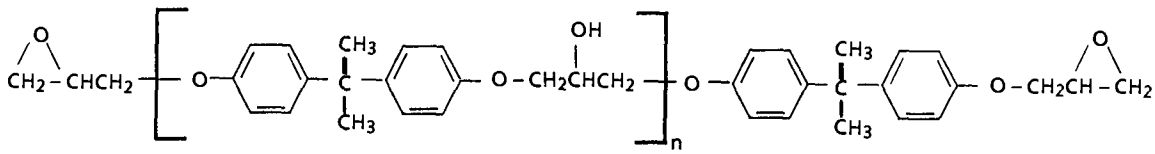

n is typically 0 to 1 for liquid resins with solid resins having n values as high as 15 or more

FIG. 1–Idealized structure of a bisphenol epoxy resin.

TABLE 1—Typical properties of bisphenol-based epoxy resins.

Average Molecular Wt	Average EEW[a]	Approximate Average Value of *n*	Viscosity, *P*, 25°C	Softening Point, °C[b]	Applications
350	182	...	80	...	Solventless and solvent-borne ambient cure coatings, electrical encapsulation, flooring, and filament winding
380	188	0.2	140	...	
600	310	1	Semisolid	40	Solvent-borne, ambient cure coatings
900	475	2	Solid	70	
1400	900	4	Solid	100	Powder coatings
2900	1850	10	Solid	130	Heat cure, solvent-borne coatings for cans, drums, primers, etc.
3750	3050	13	Solid	150	

[a]EEW = epoxide equivalent weight, i.e., grams of resins needed to provide 1 *M* equivalent of epoxide. Also referred to as WPE (weight per epoxide) and EMM (epoxy molar mass). All three terms are interchangeable.
[b]Softening point by Durran's mercury method [ASTM Specification for Epoxy Resins (D 1763)].

through reaction of the amine with the epoxy groups. Amino- and phenoplast cross-linking resins are generally etherified urea-formaldehyde, melamine-formaldehyde, and phenol-formaldehyde condensates. The amino- and phenoplast resins cure by condensation with the backbone hydroxyls of the epoxy resin with elimination of water or an alcohol.

Aliphatic amines such as ethylene diamine (EDA), diethylene triamine (DETA), and triethylene tetramine (TETA) have always been popular curing agents for epoxy resins because of their ability to readily cure at room temperature. However, aliphatic amines present certain handling hazards because of their high basicity and relatively high vapor pressure. Epoxy/amine adducts, amine-terminated polyamides, ketimines, and other modified polyamines are less hazardous derivatives of aliphatic amines and often provide performance and handling advantages.

EPOXY RESIN COATINGS

There are a number of possible ways to classify epoxy resin coatings. Since curing agent types have been divided into ambient-cure and heat-cure, for convenience the types of epoxy coatings can also be classified similarly. The bulk of the ambient-cure or "air-dry" coatings are cured with polyamines or modified polyamines and generally find application as maintenance and marine or architectural coatings. Ambient-cure coatings are based on low-molecular-weight epoxy resins having high epoxy group content and are generally cured through reaction of the epoxy group. In addition to the "two-package" type ambient cure epoxy coatings, air dry epoxy esters, prepared by esterifying epoxy resins with unsaturated fatty acids, dry by the same mechanism as alkyd resins. Historically ambient-cure coatings have been applied out of solvent, typically at about 40% weight solids. However, with the regulation of emissions of volatile organics, the trend has been toward coatings with lower volatile organic content, 100% solids, and waterborne systems.

Heat-cure coatings are used in industrial finishes, automotive primers, appliance primers, pipe coatings, and coatings for beer and beverage cans, as well as cured coatings for pails and drums. Conventional solvent-borne and waterborne heat-cured coatings are based on the higher-molecular-weight epoxy resins, and they are generally cured through reaction of the hydroxyl groups. Powder coatings, however, are generally manufactured from intermediate molecular weight solid resins and are cured through the epoxy group. The usual curing agents for heat-cured epoxy resin coatings are amino- and phenoplast resins, as well as dicyandiamide and polycarboxlic acids, which are used in powder coatings.

TWO-PACKAGE, AMBIENT-CURE COATINGS

By far the largest volume of ambient-cure epoxy resin coatings are the "two-package" type, which are typically manufactured from liquid or low-molecular-weight solid epoxy resins cured with a polyamine, amine adduct, or polyamide. A two-package coating, as the name implies, is a two-part system:

the epoxy component and the curing agent, which are packaged separately and often in volume ratios of 2 to 1 or 4 to 1 of epoxy component to curing agent. Two-package epoxy coatings are mixed just prior to application and are characterized by a limited working life or pot life after the resin and curing agent components are mixed. Commercial systems will have pot lives of a few hours to a couple of days, with typical working times of about 8 to 12 h.

Two-package epoxy resin coatings include a broad range of products and properties. Specific film properties depend on selection among many epoxy resins, curing agents, pigments, and modifiers, as well as the ratios of these materials. Resins differ primarily in molecular weight. As the molecular weight of the resin increases, the flexibility, flexibility retention, film-leveling properties, and pot life of the coating increase. However, cross-link density decreases with increasing molecular weight, resulting in reduced solvent and chemical resistance as well as nonvolatile content of the paint at application viscosity.

Although aliphatic polyamines are less expensive and have been used extensively as curing agents, polyamine adducts, amine-terminated polyamides, and ketimines are generally preferred. Among the advantages provided by aliphatic amine adducts are:

- Milder odor.
- Lower volatility.
- Less tendency to produce blush when coatings are applied under conditions of high humidity.
- Greater suitability for application at low temperature.
- Less tendency to corrode metal containers.

Two general types of polyamine adducts are available, i.e., those based on a low-molecular-weight liquid epoxy resin and those based on a high-molecular-weight solid epoxy resin. The performance properties of amine-cured coatings are not significantly different from those of aliphatic polyamine cured systems. Like polyamines, amine adducts offer maximum resistance to solvents, acids, and other highly corrosive chemicals. Initial flexibility and impact resistance are excellent, and retention of these properties is adequate for most uses over rigid or semi-rigid substrates.

More pounds of polyamide curing agents are consumed annually in the United States than any other type of epoxy resin curing agent. Polyamides are obtained from the condensation of dimerized and/or trimerized fatty acids with aliphatic polyamines such as diethylene triamine and triethylene tetramine to give an amine-terminated polyamide. Polyamide cured epoxy coatings develop superior adhesion to moist and poorly prepared surfaces, and they provide a high degree of corrosion resistance. Like epoxy resins, polyamides are also mixtures of oligomers. Thus, a range of polyamides which vary in viscosity, amine equivalent weight, and reactivity is available. Polyamide cured coatings exhibit somewhat better retention of flexibility and impact resistance on aging than polyamine adducts. Although resistance to solvents and acids is not quite as good as with other types of amine curing agents, polyamides are adequate for most applications where amine cure epoxy coatings are used.

Ketones add reversibly to primary amines with the loss of water to give ketimines. The ketimines obtained from the typical polyamine curing agents have rather low volatility compared to the precursor polyamine. Ketimine curing agents can be considered blocked polyamines, which in the presence of water hydrolyze to produce a ketone and a polyamine. These ketimines react at a practical rate of cure under ambient conditions. Atmospheric moisture, which is absorbed during and following application of the coating, serves as the source of water required to activate the curing agent. Ketimine curing agents are similar in behavior to the aliphatic amine polyamines and amine adducts in rate of cure and performance of cured films, but they provide much longer pot lives.

Typical applications of two-package coatings of the above type are in heavy-duty maintenance and marine coatings, tank linings, aircraft primers, internal pipe coatings, for gas transmission lines, coatings for plastic products, and high-performance architectural coatings.

EPOXY RESIN ESTER, AMBIENT CURE COATINGS

Epoxy resin esters are prepared by esterifying the resin with vegetable oil fatty acids. Epoxy esters are usually prepared from solid epoxy resins having EEWs in the range of 900. As in conventional alkyd technology, these coatings are made by esterifying the resin with fatty acid at temperatures of 400 to 450°F (204 to 232°C). Initially, the fatty acid reacts with the epoxy ring at lower temperatures, forming hydroxyl esters. Subsequently, these hydroxyl groups and those already present in the resin are esterified at higher temperatures with the aid of esterification catalysts and with azeotropic removal of water. Typically, between 30 and 90% esterification is chosen, depending on the oil length desired.

Like alkyd resins, epoxy resin esters may be made in long, medium, and short oil lengths. The oil length refers to the degree of esterification of the epoxy resin with the fatty acid: long indicates 70 to 90% esterification, medium indicates 50 to 70% esterification, and short indicates 30 to 50% esterification. By proper selection of acids and adjustment of reaction ratios, long, medium, or short oil esters may be prepared with drying, semidrying, or nondrying characteristics. The terms "drying" or "air dry"are used instead of ambient-cure since cross-linking of epoxy resin esters does not involve a curing agent. Air-dry epoxy resin ester coatings are "one-package" or one-component systems, since they cross-link or cure only on exposure to air.

Air-dry epoxy ester coatings are used in maintenance and marine coatings, especially where mildly corrosive conditions are encountered. They do not, however, possess the outstanding chemical resistance of amine-cured epoxy coatings, but they are superior to alkyd paints. In addition, their toughness and durability make them well suited for long-wearing floor finishes.

HEAT-CURED SOLVENT-BORNE EPOXY RESIN COATINGS

Conventional solvent-borne heat-cured or "baked" epoxy resin coatings are based on high-molecular-weight epoxy resins, that is, resins with EEWs around 1750 or greater. The concentration of epoxy groups is low in these resins, and

cross-linking occurs principally through the hydroxyl functionality. Thermosetting resins such as urea-formaldehyde, melamine-formaldehyde, and phenol-formaldehyde resins are used as cross-linkers for the coatings of this type. This cross-linking requires heat, and usually a strong acid catalyst is used to accelerate the cure. Thus, these systems are supplied as "one-component" systems, i.e., the resin, curing agent, and accelerator are packaged together.

Aminoplast (urea-formaldehyde or melamine-formaldehyde) cross-linking resins are used because of their good color and relatively low cure temperature. They are typically used in linings for beer and beverage containers and as clear coatings for brass and jewelry. Pigmented aminoplast cured coatings are used as coatings for industrial equipment, appliances, and hospital and laboratory furniture. Phenoplast (phenol-formaldehyde) cured coatings are more chemically resistant, and they find application in beer and beverage containers (particularly in Europe), drum and pail linings, internal coatings for pipe, wire coatings, and appliance primers. Phenoplast resins, generally giving coatings of poorer color than aminoplast resins, are used only when maximum resistance to solvents and other chemicals is required.

HEAT-CURED WATERBORNE EPOXY COATINGS

The earliest epoxy resin coatings for beer and beverage containers were solvent-borne amino- or phenoplast cured systems, the particular systems used being dependent on the application. Although application technology has changed over the years and is now dominated by waterborne systems, the coatings are still basically amino- or phenoplast cured systems. These coating systems are based on high-molecular-weight epoxy resins onto which are grafted terpolymers of, for example, styrene/methacrylic acid/ethyl acrylate. These epoxy/acrylic graft polymers are neutralized with base, such as dimethylethanolamine, to give a resin easily dispersible in water. The dispersed resin can then be cured with an aminoplast resin to give coatings with properties that make them suitable for beer and beverage containers.

ELECTRODEPOSITION COATINGS

Epoxy resin electrodeposition coatings are also waterborne coatings formulated from either anionic or cationic epoxy resin polymers. The part to be coated is dipped into the electrodeposition bath, and an appropriate electrical charge is applied, causing the coating to deposit onto the part. The part is then removed from the bath, rinsed, and baked to cure the coating. In the United States, epoxy-based electrodeposition coatings account for over 92% of all electrodeposition coatings. Epoxy-based cathodic electrodeposition (CED) automotive primers dominate this application, accounting for over 82% of all electrodeposition coatings. Over 40 million pounds of epoxy resin are used in the United States in CED automotive primers, making this one of the largest single end uses for epoxy resins in coatings. Virtually every automobile made in the United States, Europe, and Japan is primed with a CED primer. CED primers are used because they afford exceptional corrosion protection and because they are deposited uniformly to all areas of the automobile, even in areas which would be inaccessible to other coating application methods such as spray. Because of their major importance, the remainder of this discussion will deal with CED automotive primers.

The preparation of CED coatings generally begins by reacting a bisphenol A based liquid epoxy with bisphenol A to give an epoxy resin with an epoxy equivalent weight in the range of 500 to 1000. This epoxy resin is then reacted with a flexibilizing diol. This diol can be an aliphatic diol or a polyether diol. The principal requirement is that the diol contain primary hydroxyl functionality. These primary hydroxyls are reacted with the epoxy groups in the presence of a suitable catalyst (e.g., a tertiary amine) to form ether linkages between the epoxy and the flexibilizing diol. At this point, the resin will have an epoxy equivalent weight in the range of 1000 to 1500. The remaining epoxy functionality is then reacted with amines. Generally, secondary amines are chosen to minimize further chain extension. One favored method to accomplish this is to use a diketimine of diethylene triamine. During coating preparation, the ketimine groups decompose to give primary amines. These primary amines are fairly basic, resulting in stable dispersions at a relatively high bath pH (pH > 6). At this point, the CED resin preparation is complete. In practice, specialized CED resins are used to make the pigment grind pastes. These are developed to efficiently make stable pigment dispersions, which retain good stability in the CED coating bath.

Curing agents used are generally blocked isocyanates. These are chosen to be stable and unreactive in the coatings bath, but to unblock and cure the coating at baking temperature. An example of such a curing agent would be the reaction product of 3 mol of toluene diisocyanate with 1 mol of trimethylolpropane. This is then reacted with 3 mol of a suitable blocking agent, such as 2-ethyl-1-hexanol. Catalysts such as tin or lead salts are generally used to facilitate unblocking and coating cure. The coating is prepared by blending the resin with pigment paste, curing agent, catalysts, additives, and solvents. A low-molecular-weight organic acid, such as lactic or acetic acid, is then added to the mixture to make ammonium salts with the amine groups in the resin. This mixture is then dispersed in water to make the CED coating. Solvents may be required in the preparation of the CED resin or other components. In order to reduce the volatile organic compound content of the finished coating, it is usually subjected to a vacuum stripping step which can reduce VOC to less than 0.7 lb/gal. When the automobile is dipped into the CED bath, a negative charge is applied to it (making it the cathode) relative to counter electrodes in the bath. Electrolysis of water occurs, forming hydroxide ions in the immediate vicinity of the automobile surface. These hydroxide ions react with the ammonium ion groups in the resin near the surface, regenerating the neutral amine groups and causing the coating to be deposited onto the surface. In this way, a uniform film is applied to the entire conductive surface of the automobile. The automobile is then removed from the bath, rinsed, and baked.

EPOXY RESIN POWDER COATINGS

Powder coatings are produced by melt blending homogenous dispersions of nonvolatile solid resins, curing agents, pigments, fillers, and various additives. The dispersion is solidified by cooling, ground into a finely divided powder form, and classified for subsequent use. The resultant powder is normally electrostatically deposited onto grounded substrates and, through the application of heat, converted into very high performance thermoset films. The process of applying coating powders allows nearly 100% powder utilization and evolves almost no volatile organic compounds.

The 1970's volatiles regulations and energy concerns raised interest in powder coating technology. The real sustaining driving forces for growth, however, have been improvements in powder coating raw materials, formulations, manufacturing technology, and application equipment. The advantages for the use of powder coatings can best be summed up in the "Four E's," used by The Powder Coating Institute: (1) excellence of finish, (2) economy in use, (3) energy efficiency, and (4) environmental acceptability. The Clean Air Act, as amended in 1990, has contributed to even greater interest in the use of powder coatings to meet more stringent volatile organic requirements. Powder coatings is the fastest growing area of coatings technology. Growth rate for powder coatings in the 1990 to 1995 time frame is projected to be at 10 to 12% versus a conventional "wet" coatings rate of about 2%.

The unique characteristics of solid epoxy resins account for their choice by formulators for use in powder coatings applications. Bisphenol-A based epoxides with equivalent weights greater than about 650 are nonsintering and extremely friable. They have relatively low melt viscosity and high reactivity via the terminal oxirane functionality. The addition reaction with amines, phenolics, or carboxylic acid functional curatives allows a wide range of formulations. The primary limitations for bisphenol-A based epoxy resins in powder coatings are yellowing and loss of gloss that occur when these coatings are exposed to exterior weathering conditions.

Powder coatings are broadly divided into either "functional" or "decorative" uses. Functional coatings are normally applied at film thicknesses greater than about 3 mil and are expected to withstand some rather severe service. Examples of functional uses are coatings for exterior and interior pipe, rebar, and various electrical devices. Although decorative powder coatings are functional, these are normally used at a film thickness of 3 mil or less and are not expected to perform significantly better than baked films derived from "wet" coatings. Some examples of decorative uses are coatings for appliances, furniture, and underhood automotive parts.

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11

Phenolics

by John S. Fry[1]

DEFINITION: *a polymeric, resinous reaction product of a phenol with an aldehyde. Said products may be used alone or in formulations with other polymers to produce useful coatings.*

HISTORY

Phenolic resins, initially commercialized in 1909, were the first completely synthetic materials for the burgeoning plastics business. The expansion of several new technologies of the time, namely the electrical, communications, and automotive industries, all required and depended on new materials that had better electrical insulating properties, higher heat resistance, and improved resistance to chemicals, acids, oils, and moisture. The heat-reactive resins, developed by Dr. Leo H. Baekeland [*1*], were formulated into blends that were convenient for mass production compression moldings and satisfied the above-mentioned requirements. Improved and new items such as coil supports, commutators, distributor heads, telephone sets, vacuum tube bases, radio parts, and electrical switches all blossomed onto the market within a few years.

FIRST PHENOLIC COATINGS

Concurrent with the above developments, the nonheat-reactive phenolics or "novolak" resins were prepared as a hoped-for substitute for shellac. These resins were not as resilient as shellac and, when used alone, were not successful in coatings. However, combined with the formaldehyde donor, hexamethylene tetramine, the novolaks could be compounded into another set of thermosetting molding materials which found early use in phonograph records.

While the above-mentioned novolaks had to wait for success in coatings, the alcohol solutions of the heat-reactive resins were found, by 1911, to form excellent films when baked and cross-linked. These coatings, still in wide use today, are hard and glass-like and have excellent resistance to chemicals, acids, water, and solvents. Early applications included protective coatings for brass beds as well as other hardware items. These solution resins also initiated the manufacture of laminates, which engendered radio circuit boards and, later, printed circuit boards.

[1]Consultant, 14 Westbrook Ave., S. Somerville, NJ 08876.

CHEMISTRY

The reaction of phenol with aldehydes to produce resinous products was difficult to understand in the early years because many of said products were insoluble or infusible. After studying the variables, Baekeland at least defined the conditions to produce three stages of products: "A" stage—soluble and fusible; "B" stage—insoluble, but swellable and softenable; and "C" stage—cured to an insoluble and heat-resistant material. With the advent of modern analytical tools, the chemistry of the reactions has been more fully defined by various workers [*2,3*]. A brief description follows.

RAW MATERIALS

The commercially important phenols used in coatings resins are shown in Fig. 1. While phenol is the most common, the substituted phenols are also used to vary the solubility and reactivity properties of resins. The cresols, butyl phenol and bisphenol-A, are widely employed while the others have limited or specialty uses.

Phenol has three aldehyde reactive ring positions; the 2 and 6 carbon atoms (ortho) and the 4 position (para). Phenols with substituents in the above positions have lower functionalities and are frequently used to modify resin properties.

The aldehyde co-reactant of choice for the phenols is formaldehyde, the most reactive of those commercially available. Formaldehyde, a gas, is conveniently handled as an aqueous solution (formalin) or as a solid polymeric form known as paraform. Formaldehyde in aqueous solutions exists as hydrated glycols or low-molecular-weight glycol ethers.

$$CH_2O + H_2O \longrightarrow HOCH_2OH \cdot HOCH_2O[CH_2O]H$$

Both of the above forms of formaldehyde depolymerize on heating to supply reactive formaldehyde for the phenolic reactions. The type of reaction products and resins formed depends on the catalysts and conditions used.

BASE CATALYST

Strong base catalysts (pH above 8) produce initial reaction products such as the methylol phenols shown in Fig. 2*a*. Phenol can produce five different methylol-related species, while the substituted phenols, with lower functionality, produce fewer methylol derivatives. Further reaction causes the methylol groups to condense with other ring positions (meth-

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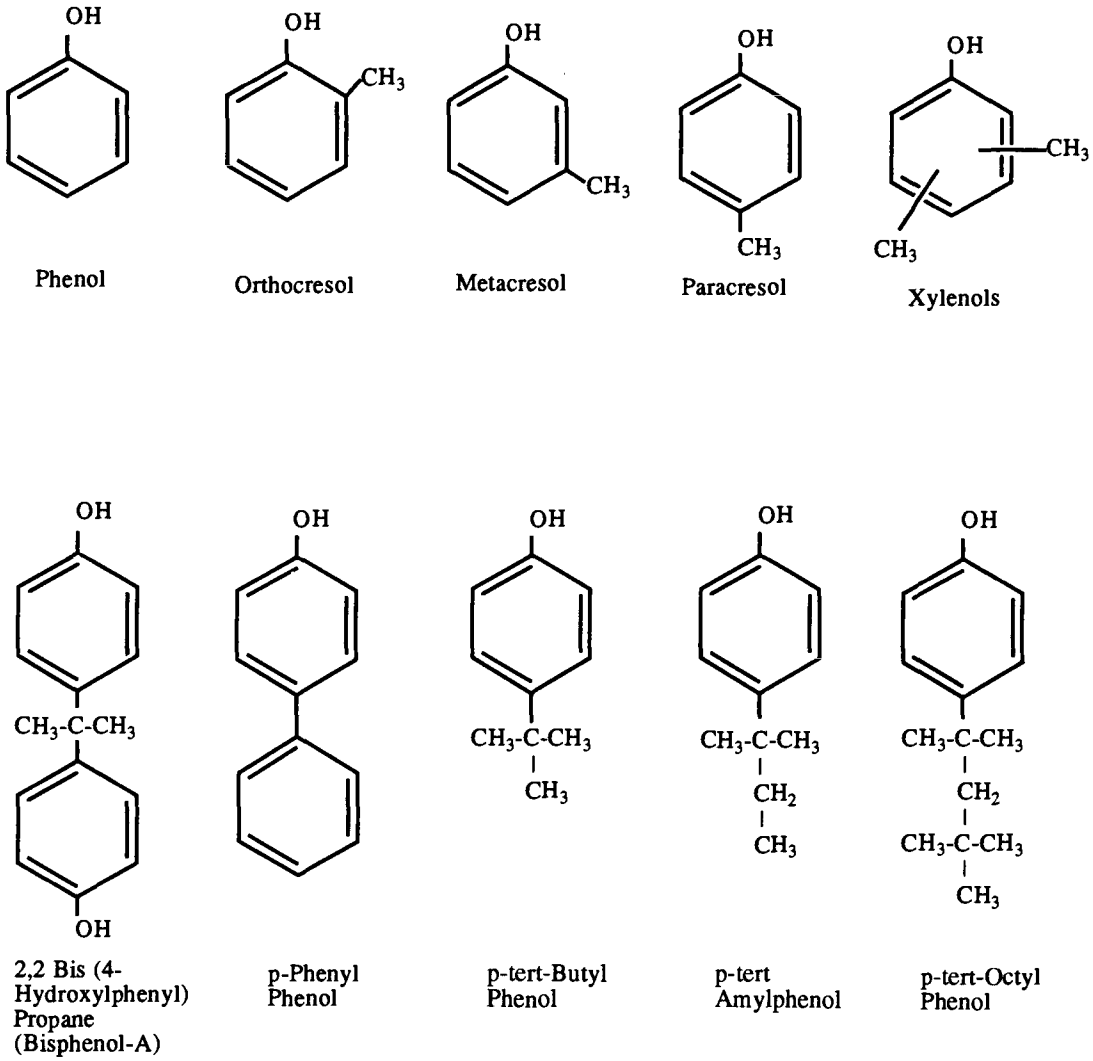

FIG. 1–Phenols used to make phenolic resins.

ylene link) or to etherify with other alcohol groups (methylene ether links) (Fig. 2*b*). Additional reaction raises the molecular weight to branched, heat-reactive resin products which are dehydrated, dissolved in solvents, or isolated as grindable solids for later formulation.

ACID CATALYST

At a pH of 0.5 to 1.5, the acid-catalyzed phenol-formaldehyde reaction proceeds through an unstable addition intermediate to condensed, methylene-linked phenolic rings (Fig. 3). When phenol is used, highly branched "novolaks" are obtained. However, when substituted phenols are used, the functionality of the system is reduced to two and mostly linear resins are formed.

INTERMEDIATE pH CATALYSIS

When salts of zinc, magnesium, or aluminum are used as catalysts, the pH of the phenol-formaldehyde reaction falls in the 4 to 7 range. Under such conditions, the formaldehyde addition to the phenolic ring is highly directed to ortho substitution. With excess formaldehyde, hemi-formals and ortho methylol groups are formed. Using lower formaldehyde levels leads to the formation of nonheat-reactive ortho-ortho novolaks. With the highly reactive para ring position still open, these resins have been employed in relatively rapid crosslinking formulations.

TESTING OF PHENOLIC RESIN PRODUCTS

Typical quality control tests for phenolic resin products may include the following.

1. Gel time [ASTM Test Method for Determining Stroke Cure Time of Thermosetting Phenol-Formaldehyde Resins (D 4640-86)] (heat-reactive resins).
2. Volatile content [ASTM Test Method for Volatile Content in Phenolic Resins (D 4639-86)].
3. Viscosity (solution).

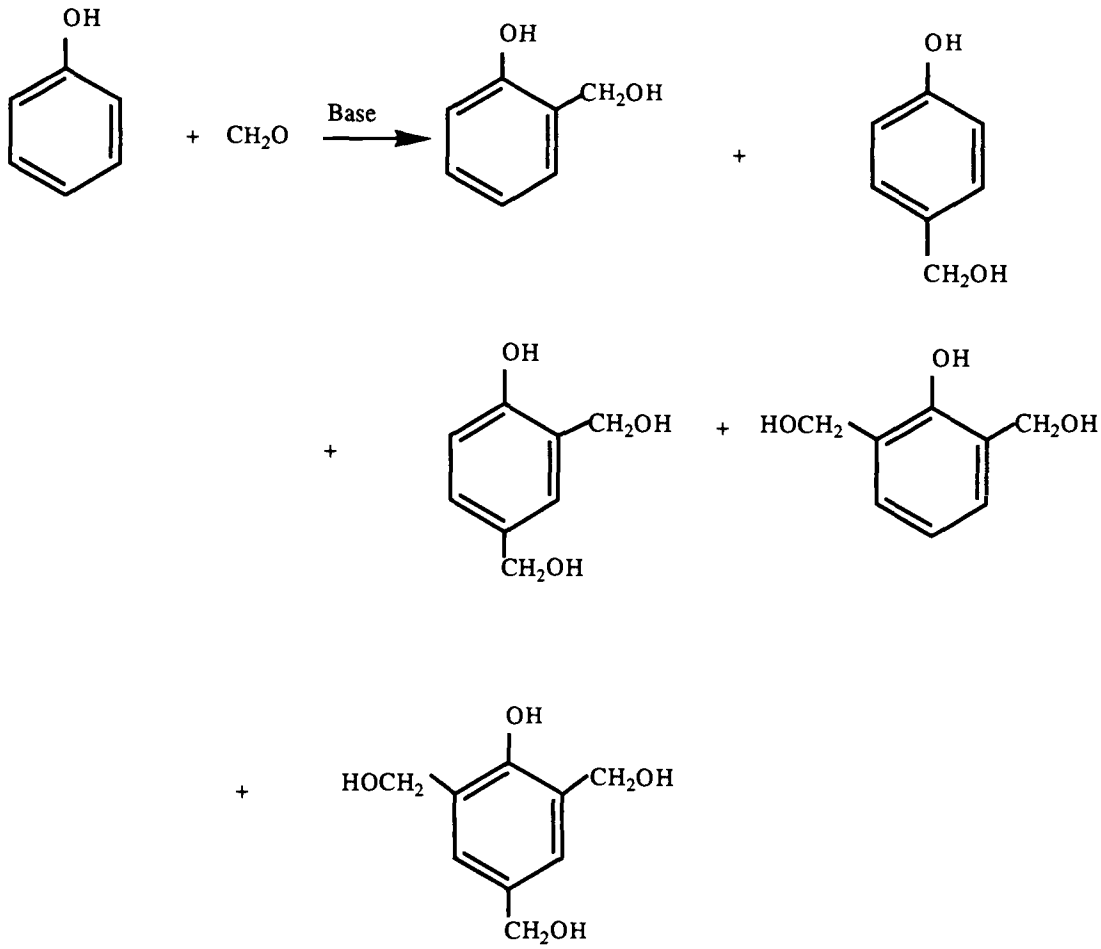

FIG. 2*a*–Base-catalyzed initial reaction products.

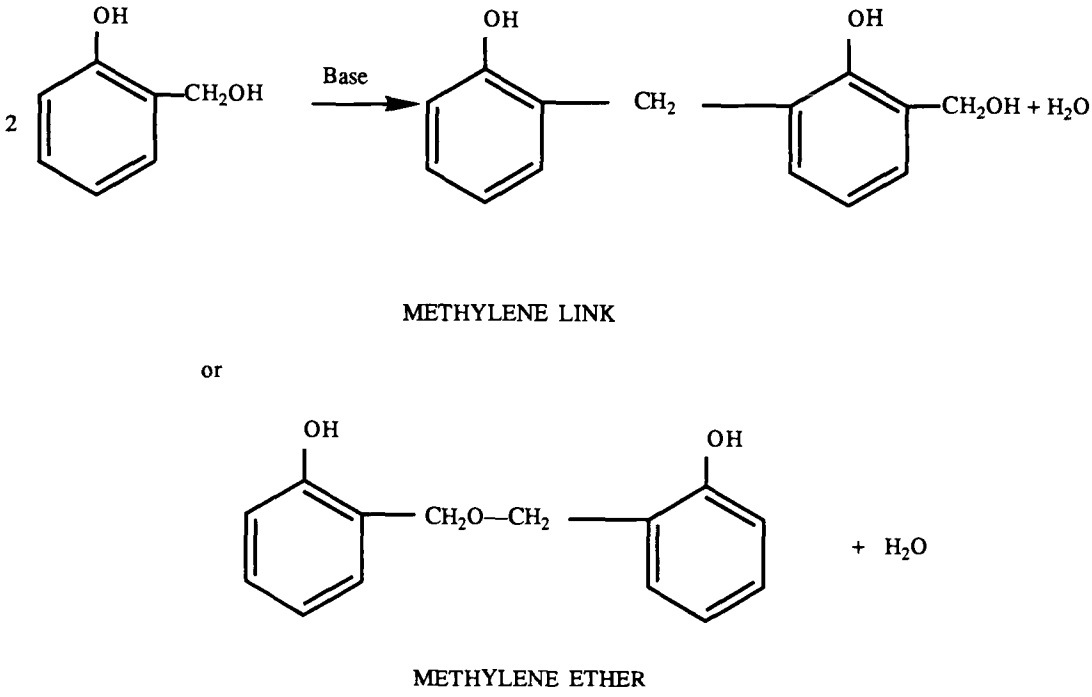

FIG. 2*b*–Methylol phenol reaction products.

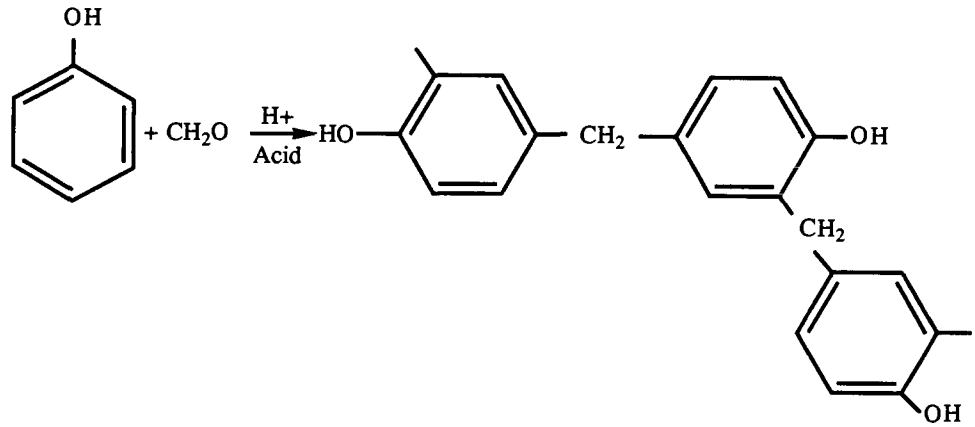

FIG. 3—Acid-catalyzed reaction products.

4. pH [ASTM Test Method for Measuring Apparent pH or Water Insoluble Phenol-Formaldehyde Resins (D 4613-86)].
5. Color (Gardner).
6. Specific gravity.

Other tests to characterize resins may be used:

1. Molecular weight distribution and free phenols—gel permeation chromatography.
2. Structure analysis—NMR, I.R.
3. Thermal analysis (curing curves).
4. Free formaldehyde–hydroxyl amine method.

HEAT REACTIVE RESINS IN COATINGS

Alcohol-Soluble Resins

The thermosetting, alcohol-soluble resins are based on multifunctional monomers such as phenol, cresols, xylenols, and bisphenol-A. These resins are also soluble in ketones, esters, and glycol ethers, but insoluble in aromatic and aliphatic hydrocarbons. They are compatible with amino resins, epoxies, polyamides, and poly(vinyl butyral) and are, in many cases, formulated with said resins as crosslinking agents. The resins are commercially available as solvent solutions, solids, or waterborne systems. Low-molecular-weight resins with a high methylol content form water solutions, while higher molecular weight resins may be used in dispersion form [*4,5*].

Once formulated into vehicles, the resins may be applied by spray, dip, brush, or roller coating methods. The films are then baked at typical temperatures of 135 to 250°C for times varying from several minutes to several hours. When used alone, phenolic resins crosslink with the release of water to form 0.2 to 1.0-mil films. Since volatiles are released during cure, bubbles may develop in thicker films. Multiple coats may be applied as long as the intermediate coats are given a short bake.

Baked phenolic coatings are hard and glass-like with excellent resistance to organic solvents, boiling water, acids, and acidic or neutral inorganic salts. They are not resistant to alkalies unless combined with epoxides as will be discussed later. These phenolic coatings have excellent electrical resistance and also resist dry heat to 370°C for short periods. As a result, these products find applications in oil industry drill pipe, production pipe, as drum and pail linings, tank linings, printing plate backing, printed circuit masks, and as corrosion-resistant hardware coatings. Tests performed on such coatings may include:

1. Electrical properties.
2. Physical and mechanical.
3. Environmental resistance.
4. Applications.

Phenolics as Crosslinking Agents for Other Polymers

Coatings based on heat-reactive phenolics alone are not very flexible. To obtain better toughness and flexibility for applications such as can coatings or coil coatings, the phenolic resins are combined with a linear resin, such as an epoxy resin, in ratios of about 15/85 to 50/50 phenolic/epoxy. Upon baking, the phenolic resin's methylol groups react with the secondary hydroxyls of the epoxy resin backbone to crosslink the system (Fig. 4). Depending on the ratio used, some of the phenolic resin may self condense, but to a lesser extent than the pictured cross-linking reaction. In the case of can coatings, thin films (0.2 mil) are applied to tin plate or tin-free steel and typically baked for 10 to 12 min at 200°C. The coated metal is then formed into can bodies and lids, and foods are then packaged. The linings have to withstand a steam sterilization cycle of about 90 min at 250°F (121°C) while protecting the metal and the food. For beer and beverage cans, phenolics based on bisphenol-A may be used to minimize critical taste effects. Similar formulations have been used for wire coatings or coil coating primers. Phenolic/epoxy systems are also more resistant to alkalies than phenolics alone and are used for linings when basic substances are packaged.

Heat-Reactive Aromatic Soluble Resins

Heat-reactive resins or copolymers based mainly on substituted phenols such as *p*-tertiary butyl phenol or those with higher alkyl groups form resins which are soluble in aromatic solvents and even tolerate some aliphatic diluents. These resins are blended with blown oils or alkyd resins to form electrical coil and armature impregnation varnishes. Such var-

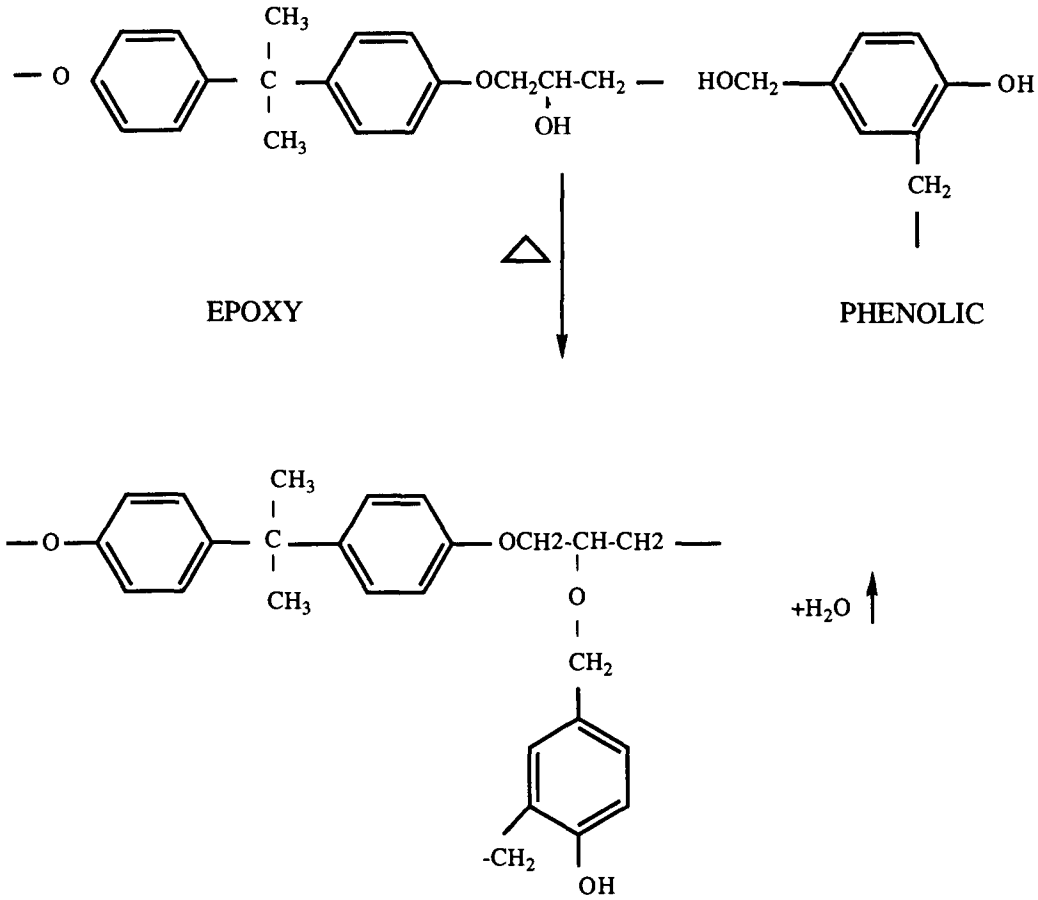

FIG. 4–Crosslink formation.

nishes may be used in both new and reconditioned electrical equipment.

Nonheat-Reactive Resins—Unsubstituted

The acid-catalyzed reaction of formaldehyde with an excess of phenol and/or cresols produces the nonheat-reactive, novolak-type resins. These resins do not form useful films by themselves, but when formulated with polyfunctional epoxy resins they act as co-reactants (hardeners) to produce thermoset systems. In this case, the chemistry involves the base-catalyzed reaction of an epoxy group with the phenolic hydroxyl group to form ether-type crosslinks which are resistant to chemicals, moisture, and heat (Fig. 5). Since this reaction does not produce by-products, thick films may be obtained via powder coatings or high solids solution coatings. Such coatings find application as pipe coatings, reinforcement bar, and electronic encapsulation coatings.

Varnish Resins

Substituted phenols containing the *tert*-butyl group or higher alkyl groups are reacted with formaldehyde under acidic conditions to produce "oil soluble" novolak resins.

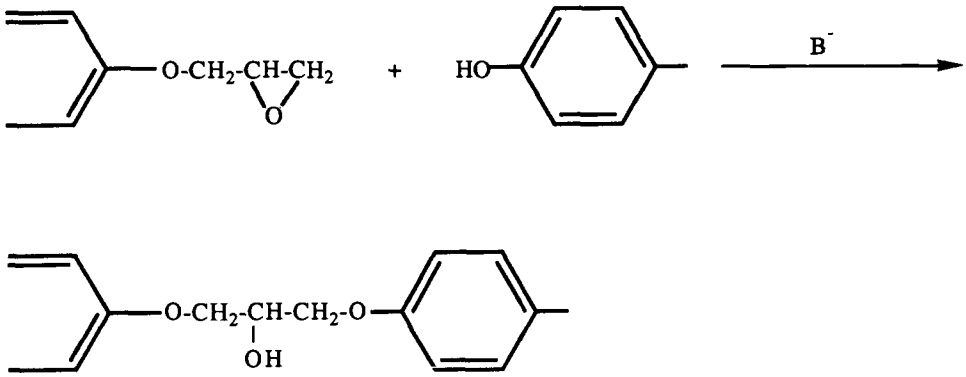

FIG. 5–Epoxy phenolic reaction.

Additionally, substituted phenols may be co-reacted with tall oil resin and formaldehyde to form modified resins, which are also "oil soluble." While they are again nonfilm formers, combined with drying oils or alkyds, the above resins produce useful air-dry or baking formulations. Varnishes based on natural oil-soluble resins and drying oils were known long before phenolic resins, but the advent of the synthetic phenolic resins led to more consistent production quality. Varnishes were originally prepared via a "cook" method where the phenolic resin was dissolved in the oils at 230 to 310°C while the oil then polymerized to a specified viscosity. After adding solvents, the varnish was cooled and then finished with additives such as driers, UV absorbers, and anti-skinning agents. In the 1950s, novel phenolic resins of higher molecular weight allowed the cold blend preparation of varnish vehicles [*6*]. In this process, the resin is dissolved in the solvents and the oils and additives are added at mild temperatures. Such vehicles are still used as baked can coatings, air drying clear wood coatings, porch and deck enamels, maintenance paints, and as alkyd reinforcements.

In the 1980s, high solids coatings were mandated by various federal and state regulations. Newer phenolic varnish resins were introduced that allowed vehicle solids of 70 to 80% to be achieved. Applied with airless spray, air drying primers and aluminum-pigmented topcoats have been successfully used for maintenance painting of major steel structures such as bridges and airport light towers [*7*].

While phenolic resin technology represents a mature field, the product class is hardly passé. Newer resins, formulations for waterborne, high solids and powder coatings, and the continued high performance in container and pipe coatings all indicate a promising future for this class of materials.

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12

Polyamides

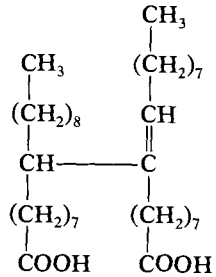
by Robert W. Kight[1]

POLYAMIDES ARE POLYCONDENSATION products of dimerized fatty acids and polyamines. Reactive polyamides are oligomers designed primarily for use in the manufacture of two-component polyamide/epoxy coatings and adhesives. The two-component coatings are generally labeled Part A and Part B, with the polyamide usually (though not always) contained in Part B. The polyamide may function as the curing agent, coreactant, or hardener for epoxy resin. Polyamides should not be considered as catalysts although they may initiate the reaction; the polyamide reacts with the epoxy resin and becomes part of the polymer. The majority of polyamides used in coatings are viscous liquids that are usually supplied by the coatings manufacturer as a solution in organic solvents. The solution may be a clear amber liquid or may contain pigments in colored systems.

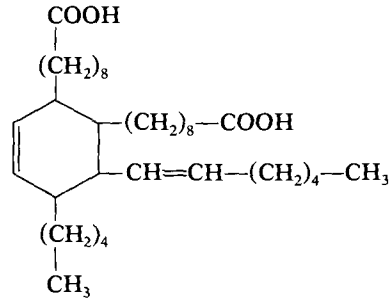
ACIDS

The dibasic fatty acids of commercial importance used to manufacture polyamide curing agents are prepared by dimerizing unsaturated C_{18} fatty acids from linseed, soya, or tall oils. Linseed and soya fatty acids are extracted from flax and soybeans, respectively. Crude tall oil (CTO) is a by-product from the Kraft process for papermaking and is a mixture of fatty acids and rosin acids, from which the fatty acids are separated by distillation. The tall oil fatty acids are a mixture of C_{18} isomers with a variable number of double bonds. Some of the isomers combine via Diels-Alder addition and other mechanisms to form C_{36} dibasic acids or dimer acids. The dimer acids produced may be acyclic, monocyclic, or polycyclic in structure, depending on the location and number of double bonds in the feedstock. Many isomers are present in commercial dimer acids, most of which are difunctional carboxylic acids [*1*]. Examples of three possible isomer types follow.

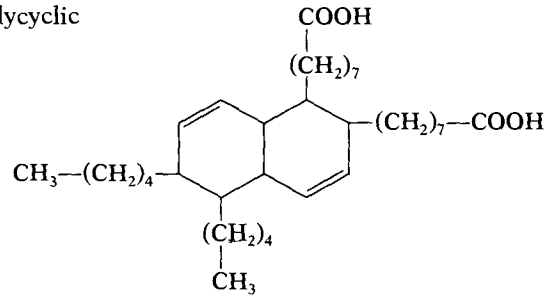
Acyclic



Monocyclic



Polycyclic

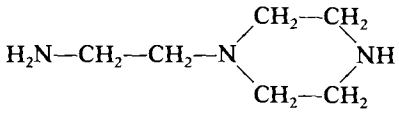


AMINES

The dimer acids are reacted with various polyamines to form polyamides and a variety of other useful products. The polyamines commonly used in industry are polyethylene polyamines of various chain lengths that are linear, branched, or cyclic. The linear polyethylene polyamines are characterized as secondary amine groups separated by ethylene chains, terminated on either end by primary amine groups. Diethylenetriamine is an example of a simple linear polyethylene polyamine.

$$H_2N—CH_2—CH_2—NH—CH_2—CH_2—NH_2$$

The cyclic and branched polyamine isomers contain tertiary amine groups in addition to the primary and secondary amine groups. Aminoethylpiperazine is an example of a cyclic polyamine.



The reaction between dimerized fatty acids and polyamines yield amide oligomers with amine group termination. These amide oligomers are used as coreactants with epoxy resins in high-performance coatings, as well as components of a variety of other useful commercial compositions including two-component adhesives.

[1]Technical Service Representative, Union Camp Corporation, P.O. Box 2668, Savannah, GA 31402.

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EARLY HISTORY

Polyamides were commercialized in the late 1950s for use with epoxy resins in the manufacture of two-component adhesives and high-performance coatings. The early commercial epoxy/amine coatings contained aliphatic amines, primarily diethylenetriamine, which had several negative features, such as requiring critical mix ratios and toxicity. The introduction of polyamides allowed the coatings manufacturer to produce high-performance coatings characterized by convenient mix ratios, such as 1:1 or 2:1, with very low toxicity.

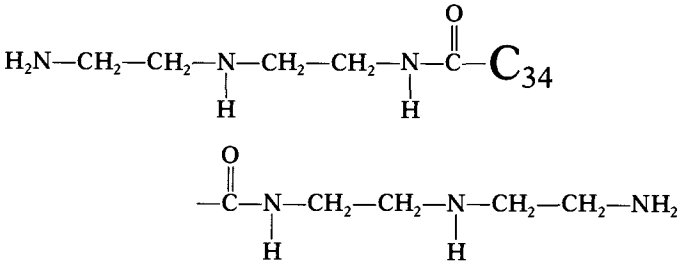
Epoxy/polyamide coatings find utility in a wide variety of applications, such as industrial maintenance coatings, machinery and equipment enamels, and marine applications. The presence of the long fatty chains gives coatings with much better flexibility as well as better wetting and adhesion than was obtained with the earlier aliphatic amine cured systems.

The epoxy/polyamide coatings are not, however, without some disadvantages. The advantage of having a long usable pot life comes with a much slower cure rate; thus epoxy/polyamide coatings generally take 8 to 10 h to reach an early cure and three to four days for a full cure. Another disadvantage is that epoxy/polyamide coatings are prone to severe chalking during exterior weathering.

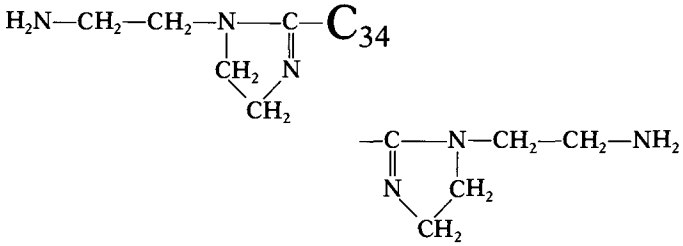
SYNTHESIS OF POLYAMIDES

Polyamides are polycondensation products of difunctional fatty acids and polyfunctional amines. In a typical commercial example, 1 mol of dimer acid is reacted with 2 mol of diethylenetriamine. During this condensation reaction, 2 mol of water are evolved. As the reaction proceeds, an interesting side reaction occurs: an additional mol or so of water evolves from a secondary reaction. One of the primary amine groups reacts with the dimer acid to form an amide linkage, which is a nitrogen bonded carbonyl. In addition, the ethylene chain next to the amide function and the secondary amine nitrogen are incorporated into a five-membered ring, known as an imidazoline ring. This condensation reaction, which also evolves water, eliminates an active hydrogen to yield a tertiary amine group. The degree of cyclization obtained is controlled to yield a product with specific useful properties, such as improved solubility and compatibility and longer pot life. Similar reactions occur at the other carboxylic acid group of the dimer [*2*]. If 50% of the diethylenetriamine present in the polyamide is cyclized to imidazoline, a total of 3 mol of water of reaction is evolved. These products are shown in the following structures:

For the polyamide



and for the imidazoline



Commercial products range from about 35% to more than 80% imidazoline to allow the coatings formulators latitude in customizing the properties of their products.

Other properties of the polyamide that are important to the coatings formulator are the amine value, which is related to active hydrogen equivalent weight, and the viscosity level of the polyamide in solvents. Amine values range from about 100 to about 400, with active hydrogen equivalent weights of about 550 to 140, respectively. The active hydrogen equivalent weight is used to calculate the amount of polyamide required to react with a given amount of an epoxy resin of known epoxide equivalent weight. The ratio of these values, known as the stoichiometric mix ratio, is most often only a starting point for the formulator. By varying the mix ratio of the polyamide to the epoxy resin, certain properties of the cured coating are enhanced (and others are sacrificed) to obtain specific application properties.

CHEMICAL PROPERTIES

The total amine value of the polyamide is determined by potentiometric titration using ASTM Test Method D 2073: Test Methods for Total, Primary, Secondary, and Tertiary Amine Values of Fatty Amines, Amidoamines, and Diamines by Referee Potentiometric Method. Note, however, that the methods specified therein for primary, secondary, and tertiary amine values are not applicable to polyamides. The total amine value is commonly listed in the specification properties of commercial polyamides and is defined as the number of milligrams of potassium hydroxide equivalent to the basicity in 1 g of sample.

The acid value, generally less than 5, that is also specified in commercial polyamides is defined as the number of milligrams of potassium hydroxide required to neutralize 1 g of sample. The acid value may be determined using ASTM Test Method D 2076: Test Methods for Acid Value and Amine Value of Fatty Quaternary Ammonium Chlorides. The procedure specified for determining the amine value in Method D 2076 is not applicable to polyamides.

The imidazoline content is not specified in commercial polyamides except in special cases where the level is deemed critical. The level of imidazoline is usually controlled by the polyamide manufacturer to provide products with specific compatibility and/or solubility. Imidazoline level can best be measured by scanning the polyamide with an infrared spectrophotometer and comparing the absorption at 6.25 μm to the absorption at 6.05 μm. The imidazoline ring absorbs at 6.25 μm, and the nitrogen-bonded carbonyl, or amide, absorbs at 6.05 μm. The result is reported as either a ratio of imidazoline:amide (I/A) or as a percentage. In the example

reaction described previously, the imidazoline ratio would be 1.0 and the percentage would be 50%.

PHYSICAL PROPERTIES

Polyamides are supplied commercially in solution or as 100% reactive liquids depending on the handling and storage requirements of the coatings manufacturer. For ease of handling, they may be supplied in various solvents. Most polyamides suitable for coatings applications are quite viscous, and these polyamides are soluble in a variety of organic solvents including alcohols, glycol ethers, ketones, and aromatic hydrocarbons. Thus the coatings manufacturer has considerable latitude in selecting specific solvents for optimum applications properties.

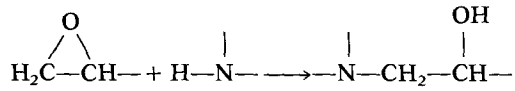
The percent nonvolatile content of polyamide solutions may be determined in accordance with ASTM Test Method D 1259: Test Method for Nonvolatile Content of Resin Solutions. Commercial polyamides are generally supplied in a single organic solvent at between 60 and 80% solids, which provides a handleable viscosity. The coatings formulator further dilutes the polyamide solution with more of the same solvent, or with a solvent blend, to form one component of the two-component system.

The polyamide component may be clear or may contain pigments in colored coatings formulations. The color of the polyamide or polyamide solution is determined in accordance with ASTM Test Method D 1544: Test Method for Color of Transparent Liquids (Gardner Color Scale).

The viscosity of the polyamide may be measured at elevated temperature in accordance with ASTM Test Method D 2196: Test Method for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield) Viscometer. The viscosity of commercial polyamides is typically specified at 75 or 150°C. The viscosity of polyamide solutions that may also be measured by this method is generally specified at 25 or 40°C. The viscosity of polyamide solutions may also be measured in accordance with ASTM Test Method D 1545: Test Method for Viscosity of Transparent Liquids by Bubble Time Method. A modification of this Method is usually used in which the polyamide solution is placed in a sample tube, the viscosity is compared to Gardner-Holdt Letter standard tubes, and the observation is reported as the alphabetic letter of the tube most closely matching the sample. A plus (+) or a minus (−) is then used to indicate that the viscosity is greater or less than the designated letter.

REACTION OF POLYAMIDES IN COATINGS

Polyamides react with epoxy resins in several stages to form a complex insoluble cross-linked matrix. The initial reaction is between the terminal primary amine groups of the polyamide and the oxirane ring of the epoxy resin. The active hydrogen opens the ring and the oligomers join end to end. This initial reaction can be represented by the following simplified structure.



The reaction of the oxirane ring and active hydrogen, which also occurs at the secondary amine sites in the polyamide, is one mechanism for the cross-linking that occurs. A secondary reaction occurs between pendant hydroxyl groups in the epoxy resin molecule and other oxirane rings present, which is another mechanism for the cross-linking reaction [3]. Because of this latter reaction it is desirable to mix the polyamide and epoxy in less than a stoichiometric ratio to provide coatings with maximum cross-link density. Such coatings will be characterized by excellent impact and chemical resistance but will tend to be less flexible. To provide more flexible coatings with greater elongation, the use of close to or greater than the stoichiometric ratio is recommended.

Polyamide/epoxy coatings contain organic solvents, which when applied appear to dry because of solvent evaporation. This early dry time is not, however, an indication of cure. Cure results from a chemcial reaction between the polyamide and epoxy resins that generally requires about 8 to 10 h before the film will resist mechanical deformation. Chemical resistance of the coating is not achieved before three to four days, and ultimate cure is achieved after about three weeks.

Polyamide/epoxy coatings may be applied by any conventional commercial applicator, including spray, brush, or roller. The coatings formulator may design the solvent system for a particular type of applicator. Polyamide/epoxy coatings may be applied to wood, concrete, or steel. For optimum adhesion to the substrate, the surface to be coated should be thoroughly cleaned and degreased. Polyamide/epoxy coatings are not normally applied to wood: when so used, the wood surfaces should be first cleaned thoroughly and any old loosely adhering paint removed. Concrete surfaces may be chemically acid etched or mechanically brushed. Steel surfaces should be sandblasted, if possible, or at a minimum should be wire brushed and chemically cleaned [4,5].

ENVIRONMENTAL/TOXICITY CONSIDERATIONS

In response to environmental concerns over the emission of organic compounds into the atmosphere, many coatings manufacturers have begun to produce high solids coatings that contain much lower levels of volatile organic compounds (VOCs). These products do not contain polyamides; instead, amidoamines are used, products formulated from monomer fatty acid rather than dimer acid [6]. A significant volume of polyamide/epoxy coatings continues to be used.

Though polyamides are less toxic than aliphatic amines and amine adducts, direct contact exposure with the skin, eyes, and the respiratory system must be avoided. Polyamide solutions must also be handled with care to avoid exposure to ignition sources as they contain flammable or combustible solvents and the vapor level from polyamide solutions must be monitored in the workplace to avoid overexposure to the organic solvents present.

Polyamide manufacturers supply material safety data sheets (MSDS), which should be consulted for hazard information and guidance on the safe use of the products. The MSDS also contains information regarding procedures to follow if a spill occurs, as well as guidelines for hazardous waste disposal. Those polyamide solutions that are classified as hazardous waste due to the presence of organic solvents must

be incinerated. Liquid (100%) polyamides are not generally classified as hazardous waste though their disposal may be regulated as an oil because of their liquid nature; these products must be either incinerated or absorbed by a suitable solid absorbent medium, such as a ground clay absorbent product, and placed in a sanitary landfill.

Though polyamides are reactive in the presence of epoxy resin, they are quite stable compounds when kept in a cool, dry environment, and they may remain unchanged for a year or more. Polyamides may be stored in drums or tanks constructed of stainless steel or aluminum. Carbon steel tanks should be avoided because of darkening of the product from iron contamination.

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[*3*] "Epoxy Resins," *Encyclopedia of Polymer Science and Engineering*, 2nd ed., John Wiley & Sons, New York, 1988, Vol. 6, pp. 348–354.

[*4*] "Polyamides from Fatty Acids," *Encyclopedia of Polymer Science and Engineering*, 2nd ed., John Wiley & Sons, New York, 1988, Vol. 11, pp. 476–489.

[*5*] Allen, R., "Epoxy Resins in Coatings," *Federation Series of Coatings Technology*, 1972, Unit 20.

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Polyurethane Coatings

by Joseph V. Koleske[1]

INTRODUCTION

THERMOPLASTIC POLYURETHANES WERE FIRST developed by Otto Bayer [*1,2*] in the Leverkusen laboratories of I. G. Farbenindustrie AG in 1937 [*3,4*] as they searched for a product that would be competitive with the polyamides, now known as nylons, that had been introduced by duPont. Shortly thereafter, Schollenberger and coworkers [*5*] used formula modification to prepare elastomeric polyurethane products from Bayer's products that were like nylon or other engineering plastics in physical characteristics.

Polyurethanes are widely used in coatings, flexible and rigid foams, elastomers, and composites. In an overall sense, the polyurethane business is huge and is concerned with rigid foams, flexible foams prepared in both slab and molded forms, elastomers, including reaction-injection-molded products, and coatings. Excluding coatings, the 1988 U.S. consumption of polyurethanes was about 2750 million lb (1.25 million metric tons) with the forecast for 1993 about 3150 million lb (1.43 million metric tons) [*6*]. In 1991, the national market for polyurethane coatings was about 209 million lb (95 000 metric tons) [*7*]. Although the market for polyurethane coatings is large and growing, it is readily apparent that it represents only about 5 to 10% of the total domestic polyurethane market. In 1991 consumption of polyurethanes for coatings in Western Europe and Japan was 301 and 100 million lb (137 000 and 46 000 metric tons), respectively [*7*]. Reasons for the use of polyurethane coatings include: high-performance characteristics such as flexibility, toughness, strength, and abrasion resistance; chemical resistance such as water, detergent, many industrial chemicals, and stain resistance; good light stability when aliphatic isocyanates are used; and low temperature-cure characteristics. The latter factor is a major reason for use of polyurethanes on plastic substrates.

DEFINITIONS

ASTM [*8*] defines *polyurethane coatings* as vehicles containing a minimum of 10% by weight on a nonvolatile vehicle basis of a multifunctional isocyanate monomer reacted in such a manner as to yield polymeric systems with urethane linkages, active isocyanate groups, or multifunctional isocyanate monomers in any ratio, proportion, or combination. Excess isocyanate groups capable of reacting at the time of application may be contained in the reaction products. ASTM has classified such polyurethanes into six general types [ASTM Terminology Relating to Paint, Varnish, Lacquer, and Related Products (D 16)] [*8*]:

Type I. "One-package prereacted" polyurethane coatings are characterized by the absence of any significant quantity of free isocyanate groups. They are usually the reaction product of a multifunctional isocyanate and a polyhydric ester of vegetable oil acids and are hardened with the aid of metallic dryers such as cobalt napthenate, manganese neodecanoate, and similar compounds. For example, linseed oil and glycerol may be first reacted and then modified with a diisocyanate that reacts with a part or all of the available hydroxyl groups. If any residual isocyanate is present, it is removed by addition of a monofunctional alcohol. Catalysts such as dibutyltin oxide and dibutyltin dilaurate are used to promote urethane-linkage formation. The coatings are also called uralkyds, urethane-modified alkyds, urethane alkyds, and oil-modified urethanes. Cure is achieved by the oxidative crosslinking of unsaturated fatty acid molecules. They are often used as automobile refinish coatings and wood and floor finishes because they provide improved scuff, water, and stain resistance over those of conventional alkyds.

Type II. "One-package, moisture cured" polyurethane coatings are isocyanate-terminated, polyester or polyether prepolymers that are capable of reacting with adventitious moisture to form mainly urea linkages between the molecules and the final coating is a polyurethane/polyurea coating. For the most part, these polyurethanes are used as clear coatings. They are often used as sealers for concrete and wood, floor finishes, and deck finishes.

Type III. "One-package, heat cured" polyurethanes cure or crosslink by thermal release of blocking agents which results in regeneration of active isocyanate groups that will subsequently react with active hydrogen groups contained in the formulation. The coatings are often used in coil coatings and electrical wire coatings.

Type IV. "Two-package catalyzed" polyurethanes are made up of one package that contains a prepolymer having free isocyanate groups and a second package that is a catalyst, initiator, accelerator, and/or crosslinking agent. Catalysts are compounds such as metal napthenates or tertiary amines. Initiators or crosslinking agents are glycols or other monomeric, multihydroxyl- or amine-functional compounds. Pot life is limited after the two packages are combined. These coatings are not widely used.

[1]Senior consultant, Consolidated Research, Inc., 1513 Brentwood Road, Charleston, WV 25314-2307.

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Type V. "Two-package polyol" polyurethanes coatings have one package that contains an isocyanate-terminated prepolymer or a multifunctional isocyanate and a second package that is made up of a polymer that contains active hydrogen groups. These relatively low molecular weight polymers are usually polyesters, polyethers, or acrylics. The second package may or may not contain a catalyst. After mixing the two packages, the systems have limited pot life. These coatings, which are high-solids in nature, are used in high performance areas such as automobile refinishes, original automotive equipment clear coats over pigmented decorative coatings, aircraft coatings, truck and bus coatings, and industrial-structure maintenance coatings.

Type VI. "One-package nonreactive lacquer" is a system that basically is a solution of a high molecular weight polyurethane (weight-average molecular weight from about 40,000 to 100,000). They are characterized by the absence of any significant quantity of free isocyanate groups, and they are converted into a solid film by solvent evaporation. The lacquers are low solids, about 10–15% by weight, in nature because of the high molecular weight involved and concomitant high viscosity of such molecules in solution. These films have very high gloss and are used in the textile industry to achieve the "wet look" that was popular in the late 1970s. They are used today for the popular cast or transfer-process fabric coatings as well as other fabric coatings.

Three other types of polyurethanes not included in the ASTM classifications are polyurethane and polyester- and polyacrylic-urethane powder coatings, ultraviolet light-curable urethanes, and waterborne urethanes [7]. The first two types have been considered as energy-activated materials and thus related to the ASTM Type III coatings.

CHEMISTRY

As with many phases of chemistry, one can consider the chemistry of urethane coatings in a simple or a complex manner. Simplistically, urethane coatings contain urethane linkages, —NHCO—, that are formed through a rearrangement reaction when an hydroxyl group reacts with an isocyanate group and that can be represented with monofunctional materials as follows

$$\mathrm{ROH} + \mathrm{R'NCO} \longrightarrow \mathrm{RO{-}\underset{\underset{\mathrm{O}}{\|}}{C}{-}\underset{\underset{\mathrm{H}}{|}}{N}R'}$$

In actual practice, functionalities of two or greater are usually involved. In addition, there are many ramifications of this reaction that will lead to the polyurethane products currently in use. It is interesting to note that urethane formation takes place through a rearrangement reaction and that no by-products are formed. The following information is meant to give the reader a brief excursion into the raw materials and some of the reactions that are important to polyurethane chemistry. Other linking groups that may be found in polyurethane coatings are allophanate, urea, biuret, and isocyanurate groups. These linkages will be discussed later.

Raw Materials

Isocyanates

Two types of isocyanates are used in coatings—aliphatic and aromatic. Polyurethanes prepared from either type isocyanate have excellent chemical and physical properties. Aromatic isocyanates are used in products where weathering resistance, particularly sunlight or ultraviolet light resistance, is not important because of discoloration, which almost always manifests itself as yellowing. Yellowing in itself is a loss of an aesthetic property, but its cause and result do not deleteriously affect mechanical properties. Ultraviolet light attacks the labile hydrogen atoms on the aromatic ring structure. Aliphatic isocyanates are less reactive and more costly than aromatic isocyanates and, while these factors can be cost considerations, aliphatic isocyanates are widely used for both interior and exterior applications.

The two main aliphatic isocyanates currently used are 4,4'-diphenylmethane diisocyanate (MDI) and toluene diisocyanate (TDI), which is a mixture of the 2,4- and 2,6-isomers. Moisture-cure urethanes and urethane alkyds usually employ TDI, though MDI has some use due to its low vapor pressure. Xylylene diisocyanate (XDI) is used to some extent, but mainly in Japan. Recently tetramethylxylylene diisocyanate (TMXDI) and isopropenyl dimethyltoluene diisocyanate (TMI) have been introduced by American Cyanamid. Naphthalene diisocyanate has also been used.

Aliphatic isocyanates are more costly, and they are used for urethane coatings that require excellent sunlight resistance and no discoloration. These coatings are used on plastics, automobiles, signs, and similar outdoor end-use products. The main aliphatic isocyanates are hydrogenated MDI (4,4'dicyclohexylmethane diisocyanate, HMDI, or H_{12}MDI), hexamethylene diisocyanate (HDI), particularly in a biuret or trimer form for improved vapor pressure, mixtures of 2,2,4- and 2,4-4-trimethyl hexamethylene diisocyanate (TMHDI), 1,4-cyclohexane diisocyanate (CHDI), and isophorone diisocyanate (3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate or IPDI) [9]. IPDI and H_{12}MDI are the isocyanates most widely used in coating preparation.

Type III polyurethane coatings, including powder coatings, employ blocked isocyanates that provide room-temperature stable, one-package systems that are activated at elevated temperatures. At elevated temperatures, the molecules dissociate and the blocking group leaves, freeing the isocyanate functionality that then readily reacts due to its nature and the kinetic effect of elevated temperature with available active hydrogen groups. Blocking groups are proton donors such as ϵ-caprolactam, malonic, and acetoacetic esters as well as other enolizable esters, ketoximes, phenol, etc. For example, trimethylolpropane (TMP) can be reacted with TDI and then blocked by reacting the free isocyanate groups with phenol:

$$\underset{\text{TMP}}{\mathrm{C_2H_5C(CH_2OH)_3}} + \underset{\text{TDI}}{\mathrm{C_6H_3(CH_3)(NCO)_2}} \longrightarrow \underset{\text{ISOCYANATE-TERMINATED ADDUCT}}{\mathrm{C_2H_5C(CH_2OCONH{-}C_6H_3(CH_3){-}NCO)_3}}$$

$$\underset{\text{ISOCYANATE-TERMINATED ADDUCT}}{\mathrm{C_2H_5C(CH_2OCONH{-}C_6H_3(CH_3){-}NCO)_3}} + \underset{\text{PHENOL}}{\mathrm{3\ C_6H_5{-}OH}} \longrightarrow \underset{\text{PHENOL-BLOCKED TRIISOCYANATE}}{\mathrm{C_2H_5C(CH_2OCONH{-}C_6H_3(CH_3){-}NHOCOC_6H_5)_3}}$$

Technology such as this is used in polyurethane powder coatings.

Active Hydrogen Sources

Isocyanates readily react with active hydrogen sources such as hydroxyl groups and amines. Hydroxyl groups are usually supplied by polyfunctional compounds such as glycols, triols, tetraols, polyester polyols, polyether polyols, acrylic polyols, and polylactone polyols. Polyether polyols are usually poly(propylene oxide) polyols that may or may not be copolymerized with ethylene oxide in a random manner or in an end-capping manner to provide primary hydroxyl end groups. These polyols, which are described in detail elsewhere in the manual, are usually di- or trihydroxyl functional compounds, though higher functionalities are used in special cases, that have number-average molecular weights of from about 200 to 3000. Polyols function as soft segments and impart flexibility to polyurethanes [*10*]. As would be expected, primary hydroxyl groups react much more rapidly than secondary hydroxyl groups, and tertiary hydroxyl groups react slower than either other type. For example, primary hydroxyl groups reacted about 3.5 faster with phenyl isocyanate than secondary hydroxyl groups and about 200 times faster than tertiary hydroxyl groups [*11*]. It was also found that *n*-butanol reacted five times faster with the isocyanate group in the para- or 4-position group than with the isocyanate next to the methyl group in 2,4-toluene diisocyanate. This demonstrated that neighboring groups can significantly affect isocyanate reactivity.

Low-molecular-weight or monomeric compounds are used as chain extenders when preparing polyurethanes [*12*], and these chain extenders in combination with the isocyanates are termed "hard segments" that function as pseudocrosslinks [*13*]. In high-molecular-weight polyurethanes, such as those used for Type VI products, these chain extenders represent only a few percent of the total polymer molecular weight yet play a significant role in final physical properties. Glycols and low-molecular-weight triols require relatively large amounts of isocyanates, usually the most costly ingredient, and impart hardness and rigidity to the final coating. These compounds are also used as initiators for preparation of the various polyols with glycerol often used for poly(propylene oxide) polyols and with glycols and triols such as 1,4-butanediol, diethylene glycol, trimethylolpropane, and the like, often used for polylactone polyols. Polyesters other than polylactones are prepared from difunctional carboxylic acids, particularly adipic acid, and glycols, particularly ethylene glycol, diethylene glycol, butanediols, and 1,6-hexanediol. An excess of glycol is used to ensure that most end groups in the polyester are hydroxyl groups. Acrylic polyols are prepared from hydroxy functional compounds, particularly 2-hydroxyl ethyl and 2-hydroxypropyl acrylate and methacrylate, other acrylates and methacrylates, and other ethylenically unsaturated, copolymerizable monomers. Examples of such monomers are ethyl acrylate, butyl acrylate, styrene, vinyl esters, etc. Epoxide, silicone, vinyl, phenolic, and oligomers that contain hydroxyl groups are also reacted with isocyanates to form urethane linkages and accompany property enhancement in specialty finishes. The epoxide, vinyl, and phenolic-based materials have good chemical resistance, and the silicone-based materials have good thermal resistance.

Polyfunctional amines, which form urea linkages with isocyanates, are also used as chain extenders. Low-molecular-weight compounds such as ethylenediamine are used as chain extenders to make polymers for Type VI lacquers. Amine-terminated oligomers based on the alkylene oxides are available [*14–16*].

Catalysts

Catalysts are often used to promote the reaction between isocyanates and hydroxyl-containing compounds. Only small amounts, on the order of 10 to 100 parts per million, of catalyst are needed to cause marked increases in reaction rate. Popular catalysts include dibutyltin dilaurate, stannous octoate, and zinc octoate. Diaza(2.2.2)bicyclooctane (DABCO), dibutyltin diacetate, bismuth stearate, and zirconium octoate have been used.

Reactions

As indicated above, hydroxyl groups react with isocyanates to form polyurethanes. Multifunctional reactants are used to link molecules as in Type I urethane alkyd [*17*] to cause molecular chain length increase in either a prereaction to form the final polyurethane that could be used in a Type VI lacquer coating or to form prepolymers that are later reacted in two-package coatings as would be used in Type IV and Type V coatings. In other instances, multifunctional (usually difunctional) isocyanates are used to end cap diols, triols, and tetraols with isocyanate functionality as is needed for Type II, IV, and V coatings. Both hydroxyl-functional and isocyanate functional prepolymers are used. For example:

$$\underset{\text{DIOL}}{\text{HO—R—OH}} + \underset{\text{DIISOCYANATE}}{2\,\text{OCN—R'—NCO}} \longrightarrow \underset{\text{ISOCYANATE-TERMINATED PREPOLYMER}}{\text{OCN—R'NHCOO—R—OOCNHR'—NCO}}$$

$$\underset{\text{DIOL}}{2\,\text{HO—R—OH}} + \underset{\text{DIISOCYANATE}}{\text{OCN—R'—NCO}} \longrightarrow \underset{\text{HYDROXYL-TERMINATED PREPOLYMER}}{\text{HO—R—OOCNH—R'NHCOO—R—OH}}$$

Other prepolymers can be prepared by reacting, for example, an hydroxyl-terminated prepolymer with two molecules of diisocyanate to produce an isocyanate-terminated prepolymer that contains urethane linkages in the central portion of the prepolymer. It should be apparent that this method of chain extension cannot be carried too far since viscosity will increase very rapidly as chain extension takes place, which is not a desirable result if materials for high-solids or other energy-conserving formulations are produced.

Moisture-cure polyurethanes are molecules with free isocyanate end groups. Sufficient quantities of isocyanate are reacted with polyols such that there are more equivalents of isocyanate groups compared to hydroxyl groups. For example, a trifunctional oligomer or polyol can be reacted with an isocyanate under moisture-free conditions and then packaged under moisture-free conditions.

$$\text{OLIGOMER(OH)}_3 + 3\,\text{R'(NCO)}_2 \longrightarrow \text{OLIGOMER(O—CONHR'NCO)}_3$$

Exact ratios of hydroxyl to isocyanate are seldom used, and final free isocyanate content usually ranges between about 3 and 16% [7]. Moisture-free conditions are achieved by blanketing the system during preparation and storage with dry nitrogen. Since these products are almost always prepared in solution, the solvent used for the reaction and for any dilution to final product must be carefully dried to exclude moisture. Solvent drying can be done with molecular sieves. When applied to a substrate and contacted with ambient moisture, these products cure by reaction with water to form an unstable carbamic acid intermediate that dissociates into an amine and carbon dioxide. The amine in turn rapidly reacts with isocyanate to form a urea linking group. This can be described by the following reaction scheme:

$$-R'NCO + H_2O \longrightarrow \underset{\text{CARBAMIC ACID, AN UNSTABLE INTERMEDIATE}}{[-R'NHCOOH]} \longrightarrow -R'NH_2 + CO_2 \uparrow$$

$$-R'NCO + -R'NH_2 \longrightarrow \underset{\text{UREA LINKAGE}}{-R'NHCONHR'-}$$

$$-R'NCO + -R'NHCONHR'- \longrightarrow \underset{\text{BIURET LINKAGE}}{-R'NHCON(CONHR-)R'-}$$

The first reactions leading to urea linkages predominate. These systems cure relatively slowly, which allows time for the evolved carbon dioxide to leave before it is undesirably entrapped in the solidifying film. Biuret linkages are formed in thermally accelerated systems, particularly at 100°C or higher, and they contribute to cross-linking (note that biurets can be equivalent to trifunctional isocyanates). Even though these cured films, strictly speaking, are urethane/urea polymers, they are usually referred to as polyurethanes.

Isocyanates will also react with urethanes to produce allophanate linkages.

$$-R'NCO + -R'NHCOOR'- \longrightarrow \underset{\text{AN ALLOPHANATE LINKAGE}}{-R'N(CONHR'-)COOR'-}$$

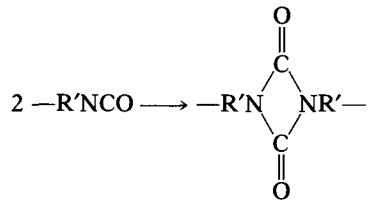
Isocyanates are less reactive with urethanes than with ureas, and temperatures of about 120 to 140°C are required to give a significant reaction rate for the formation of allophanate linkages. Allophanate formation results in branching in the polymeric network.

Carboxylic acids will react with isocyanates to form unstable mixed anhydrides that decompose into an amide and carbon dioxide.

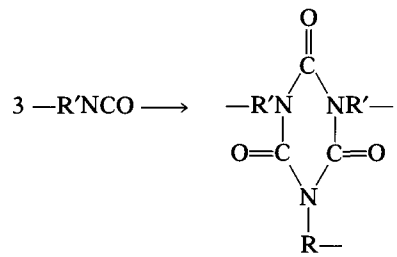
$$R'NCO + RCOOH \longrightarrow \underset{\text{MIXED ANHYDRIDE}}{R'NHCOOCOR} \; 2 \longrightarrow \underset{\text{AMIDE}}{R'NHCOR} + CO_2 \uparrow$$

This reaction is important to keep in mind when polyesters prepared from glycols and dicarboxylic acids are used or when acid numbers are unexpectedly high in polyether, polylactone, or other polyols. The end product of this reaction results in stoppage of chain growth and a lower than expected molecular weight. In most cases this is undesirable. Amides will react with isocyanates to form acyl ureas.

Isocyanates will dimerize (aromatic) to form uretidine diones and trimerize (aromatic and aliphatic) to form isocyanurates. These reactions decrease the expected equivalent weight of isocyanates, a cost factor, and will lead to branching, cross-linking, and unexpected molecular weight increases which often are undesirable in various polyurethane formulations.



URETIDINE DIONE



ISOCYANURATE

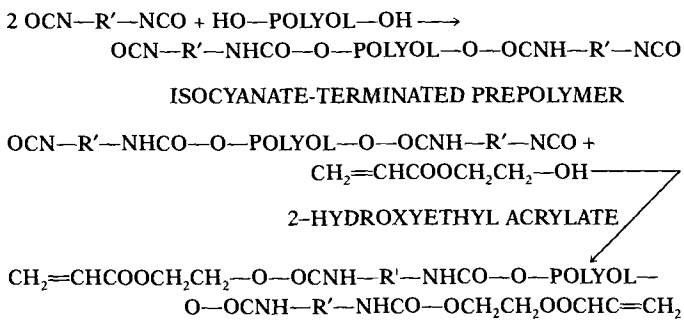
Thermoplastic Polyurethanes

Thermoplastic polyurethanes are used in Type VI lacquers and in many industrial end uses that require solid products. Their chemistry is similar to that of prepolymers except short-chain extenders are used to connect the prepolymer molecules and build them into long polymeric materials. In a structural sense, they may be described as linear block copolymers of the AB_n type. One of the blocks is a relatively long, number-average molecular weight of about 300 to 3000, polyether or polyester that forms the soft or flexible segment. The other block is formed by the reaction of a diisocyanate and a low-molecular-weight diol chain extender. The polar nature of the urethane linkages in the hard segment results in hard segment aggregation and domain segregation from the soft segment. The hard segments act as pseudo cross-links, and as a result tough, strong, elastomeric macromolecules are formed.

In a mole sense, these polymers can be viewed as polyol/diisocyanate/short-chain extender polymers that are formed in an equivalents ratio of $1/X/(X - 1)$. The number X can vary from 1 or less to as much as 20 or more, though more typically in coatings X has a value of one or less to about 3 or 4 [*10,13*]. Because of solubility characteristics, a ratio of about 1/2/1 is often used. A small excess of hydroxyl groups is used to keep final free isocyanate content and storage reactivity at a nil level. When the wide range of values of X, the types of isocyanates, the types and functionalities of polyols, and the range of polyol molecular weight available is considered, it is readily apparent that a myriad of polyurethanes can be prepared and that a broad range of mechanical and chemical properties can be achieved. The chemistry is basically isocyanates reacting with hydroxyl groups to form urethane linkages.

Radiation-Curable Urethanes [18–20]

Acrylate-terminated polyurethanes are used in a number of ultraviolet light and electron beam curable formulations. The products are termed "urethane acrylates" or "acrylated urethanes." They are prepared by first forming an isocyanate-terminated prepolymer from a polyol and then end capping the prepolymer with an hydroxy acrylate such as 2-hydroxyethyl acrylate. The reactions leading to urethane acrylates are almost always carried out in an inert solvent.

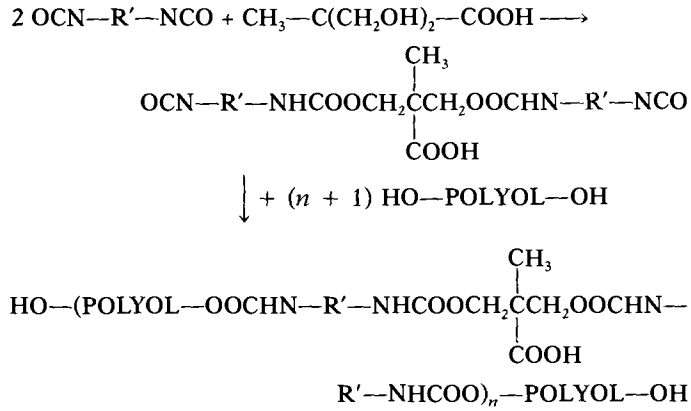


The reactions as depicted above have been idealized. In all commercial and most laboratory preparations there is a significant amount of reaction between the ingredients so that chain extension occurs and molecular weight increases. This causes the final product to have a markedly higher-than-expected viscosity. Oligomeric compounds such as these are formulated with triacrylates such as trimethylolpropane triacrylate to provide cross-linking, monomeric acrylates, N-vinyl pyrrolidone, or other compounds for viscosity reduction to provide low-viscosity, essentially 100% solids systems that will cure when exposed to actinic radiation. In formulations, the urethane acrylate is considered as the main ingredient contributing to mechanical properties of the cured film. When the actinic radiation source is ultraviolet light, a photoinitiator (for example, 2,2-diethoxyacetophenone or benzophenone in combination with an amine synergist, etc.) is added as a free radical source. Electron beam curable formulations do not require a photoinitiator.

Radiation-cured polyurethanes are often used on plastic substrates that require only low or moderate curing temperatures such as clear overprint lacquers on vinyl decals, electronic circuit boards, "no wax" vinyl flooring, and tile. Although radiation-cured colored and pigmented inks and coatings are used in the marketplace, the skill needed in preparing such products, because of difficulty with light penetration or absorption, is readily apparent.

Water-Borne Polyurethanes

Water-borne polyurethanes are prepared in bulk or in a solvent by first preparing an ionomer prepolymer that is neutralized and then chain extended to a desired molecular weight. The polymer then is dispersed into water. Both cationic [21,22] and anionic [23,24] systems are known. Cationic systems employ an amine-containing diol such as diethanolamine, methyl diethanolamine, *N,N*-bis(hydroxyethyl)-α-aminopyridine, lysine, *N*-hydroxyethylpiperidine, and similar compounds. Anionic systems use a carboxylic acid-containing diol such as dimethylolpropionic acid (2,2-bis(hydroxymethyl) propionic acid), dihydroxybenzoic acid, sulfonic acids as 2-hydroxymethyl-3-hydroxypropanesulfonic acid, and similar compounds. For example:



Water-borne polyurethane laminating adhesives that are completely free of volatile organic compounds are expected to be the next developments in this area [25]. These adhesives are expected to be for the low-to-medium demand product area such as for snack food and similar packaged products.

Powder Coatings

Polyurethane powder coatings are usually urethane-modified polyesters and polyacrylics that cure at high temperatures. High temperatures are needed for the powdered polymer to flow and level to the extent needed for a particular end use. The key to successful powder coatings is related to a balance between molecular weight and related viscosity and a cross-linking mechanism that is stable under storage conditions and not effected to any significant degree until flow and leveling takes place at the cure temperature. Another requirement is that the glass transition temperature should be sufficiently high that the powder does not block during storage. The main end use for powdered polyurethanes is in the major appliance market—refrigerators, dryer drums, range cabinets, etc.—coatings.

MARKETS

Polyurethanes of the various types are used in a number of market areas and end uses. Many of these were mentioned above. Two features of polyurethane coatings that have been often looked on as disadvantages are high cost and special handing of the potentially hazardous isocyanates that are used in manufacture or as curing agents. However, the various industry segments have been able to develop safe handling and use methods that overcome one of the objections. The very high performance characteristics of polyurethanes, their ability to cure at lower baking temperatures, and the

TABLE 1—Polyurethane end uses.

HOME FURNISHINGS	PLASTIC SUBSTRATES
Drum dryers	Fascia
Furniture	Electronic parts and equipment
"No wax" flooring and tile	Optical fibers
Range cabinets	Printed circuit boards
Refrigerators	Sheet molding compound
Wood floors	
INDUSTRIAL MAINTENANCE	RECREATIONAL PRODUCTS
Bridges	Golf balls
Industrial buildings	Golf clubs
Marine coatings	Gym floors
Plant equipment	Toys
Public utility works	
Roof coatings	TEXTILES
Windows	Apparel
	Leather
MISCELLANEOUS	Tarpaulins
Aerospace coatings	Upholstery
Luggage	
Magnetic tape coatings	TRANSPORTATION
Mast and spar finishes	Aircraft
Medical equipment	Automotive OEM
Safety glass	Automotive refinish
Shoes	Golf carts
Vinyl decal overprints	Motorcycles
Wire coatings	Railroad cars
	Trucks and buses
	Vans

improved total coating solids, i.e., decreased volatile organic compound content, that can be obtained are factors that offset their high cost. For example, polyurethanes are replacing poly(vinyl chloride) plastisols as undercoatings and sealants in the automotive and other transportation coating market. Lower coating thickness and equivalent or improved performance make the applied cost of the polyurethane competitive with the plastisol. The textile area is a moderate growth area for thermoplastic polyurethane lacquers with the excellent combination of properties as the main driving force for use. These include good elasticity at low temperatures, abrasion resistance, solvent and water resistance, dry cleanability, machine washability, and an ability to be prepared in a broad variety of tensile/elongation properties. In addition, the high performance can be achieved with very thin coatings that do not markedly increase fabric weight or change styling factors such as drape. To decrease volatile organic content, new low-viscosity, aliphatic isocyanates [*26*] and polyurethane polyols [*27*] are being developed. Although it is not a complete listing, Table 1 is a summary of many end uses for polyurethane coatings.

In the five-year period between 1991 and 1996, it is estimated that the U.S. polyurethane coating market will grow at a compounded annual rate of 5% or from 209 million lb to 265 million lb (95 000 to 123 400 metric tons) [*7*]. It is expected that the two-package (ASTM Type IV and V) systems will have almost double the compounded annual growth rate of the overall urethane coating market, i.e., about 10%, with consumption rising from 84 million lb in 1991 to 133 million lb in 1996 (38 200 to 60 500 metric tons). Waterborne and powdered polyurethanes are also important growth areas.

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14

Silicone Coatings

by D. J. Petraitis[1]

UNIQUE PROPERTIES OF SILICONES THAT MAKE THEM USEFUL AS COATINGS

Silicone based coatings are among the most useful materials for a wide variety of applications. Because the basic bond energies of Si—C and Si—O bonds are so high, the chemical processes usually associated with aging of coated surfaces are often much slower and in many situations virtually eliminated for silicone coatings. Also, because the Si—O and Si—C bonds are not present in the natural organic world, biocompatibility and resistance to degradation via biochemical and biophysical processes are also significantly reduced. In a similar manner, some silicone resinous coatings and fluorosilicone based coatings, in particular, have excellent solvent resistance.

Silicone coatings based on trifluoropropyl methyl polysiloxanes have resistance to swelling from such agents as gasoline, jet fuel, solvents, and various other reagents. Highly branched resinous silicone coatings chemically begin to approach the properties of silica surfaces as the organic pendant content is reduced. As the organic pendant groups are reduced, the $SiO_{4/2}$ content increases and the chemical resistance increases. Such resinous coatings can provide physical scratch resistance as well as chemical resistance. Silicone elastomeric coatings, however, do not provide good resistance to strong acids and/or bases. Strong acids or bases, in particular at elevated temperatures, can cause depolymerization of the siloxane backbone, resulting in failure, or in the case of silicone elastomeric coatings, dissolution of the coating itself.

In a similar manner, silicone coatings are resistant to virtually all frequencies of the electromagnetic spectrum. For complaint coatings, silicones are unsurpassed in resistance to hard radiation, such as that from a cobalt-60 source for doses in excess of 20 Mrd, as well as the ultraviolet and infrared frequencies. When combined with their hydrophobicity and oxygen and ozone resistant properties, silicones provide excellent weatherability characteristics, and when these properties are combined with the resistance to atomic oxygen in low earth orbit, silicone coatings provide protection for organic substrates in varied spacecraft applications.

Another family of applications which combine the chemical and biochemical characteristics of silicones are those which are used to provide coatings for medical devices. Silicone coatings are used to encapsulate and seal permanent implants such as heart pacemakers. They have also been used to coat temporary implants such as catheters and surgical drains. Also, thin silicone elastomer coatings are used to provide soft tissue replacements by forming an envelope to encapsulate gels and/or normal saline solutions. Recent applications for biocompatible silicone coatings include drug delivery devices for both transdermal and long-term implantable, controlled-release drug delivery.

A final characteristic which makes silicone coatings useful is their inherently low or nonflammability. Typically, silicone elastomer coatings have been rated SE-1 when tested via Underwriters' Laboratories Flame Test (UL-94). This property makes silicone coatings ideal for conformal coating of various electrical circuits and devices. In the event of catastrophic thermal degradation, the silicone coatings can and do provide an SiO_2 ash coating which may permit the emergency operation of the electrical device on a short-term temporary basis.

FORMS OF SILICONE COATINGS

Silicone coatings are available in various forms ranging from a hard, rigid resin to a compliant elastomer to a soft, almost gel-like character. The rigid resins are typically supplied in a solvent solution and are mixed with curing agents prior to application. Among the most common curing agents are lead and zinc octoate, which require approximately 1 h at 250°C to attain complete cure. The cross-linking mechanism involves the condensation of silanol groups

$$\equiv SiOH + HOSi\equiv \longrightarrow \equiv SiOSi\equiv + H_2O$$

Specific coating applications include jet engine components, furnace parts, incinerators, high-temperature appliances, and missile coatings. In addition, specific silicone resins have been designed to mix with organic coatings and paints, providing higher performance under moderate heat environments.

By varying the R group:Si ratio, the hardness of the final coatings can be varied. As the R:Si ratio is decreased, the cross-link density of the resin effectively increases. Similarly, variation of the R group itself can result in somewhat different flexibility and other properties. Properly designed and condensed resins can be formulated to provide hard silica-like abrasion-resistant coatings. Such coatings often involve the condensation of alkoxy groups with silanol groups as well as condensation between silanol groups alone. Technology to minimize shrink and maximize adhesion during the cure

[1]Vice president, Operations, NuSil Technology, 1040 Cindy Lane, Carpinteria, CA 93013.

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needs to be incorporated to prevent cracking and subsequent flaking of the coating from the substrate. Aminofunctional alkoxy silanes are often incorporated into the formulation to simultaneously optimize cure rate and adhesion.

Silicone elastomeric coatings incorporate the use of polymeric siloxanes with appropriate cross-linkers to provide compliant, flexible coatings. Among the cure mechanisms which result in elastomers are the following

1. $\equiv SiOH + HSi\equiv \xrightarrow{Sn} \equiv SiOSi\equiv + H_2$
2. $\equiv SiOH + CH_3COOSi\equiv \xrightarrow[H_2O]{Sn} \equiv SiOSi\equiv + CH_3COOH$
3. $\equiv SiOH + ROSi\equiv \xrightarrow{Sn} \equiv SiOSi\equiv + ROH$
4. $\equiv SiCH{=}CH_2 + HSi\equiv \xrightarrow{Pt} \equiv SiCH_2CH_2Si\equiv$
5. $\equiv SiOH + R_2NOSi\equiv \xrightarrow[H_2O]{Sn} \equiv SiOSi\equiv + R_2NOH$

These elastomeric coatings can range from extremely tough, high-strength elastomers to soft gel-like coatings. Typically, the elastomer could have properties within the following ranges:

Durometer:	Type 00 = 10
	Type A = 70
Tensile Strength:	0.34 to 13.8 MPa
Elongation:	50 to 1500%
Tear Strength:	0.88 to 43.8 kN/m

The properties and the cure systems which are chosen for these elastomeric coatings depend, to a large extent, on the end use and the method of application. For instance, the SiOH + HSi (No. 1) mechanism is often used to provide release coatings for backing paper for pressure sensitive adhesives. The actual coating itself has poor strength but attains its properties by simply impregnating the substrate.

The acetoxy cure system (No. 2) is used where one-part convenience is desired, where relatively slow cure is acceptable, and where acetic acid given off during the cure is not a problem.

The oxime (No. 5) cure system provides many of the properties of the acetoxy cure system, but results in an oxime leaving group instead of an acetic acid leaving group. Among the applications for the oxime cure systems are coatings for electronic components and protection for organic composites to prevent atomic oxygen degradation, and coating of quartz blankets to provide adequate emissivity and reflectivity characteristics for certain thermal protection surfaces on the space shuttle. The alkoxy 2-part (No. 3) cure system, when combined with certain thermal enhancing fillers such as iron oxide, glass microballoons, and various fibers, is often used to provide ablative and thermally insulating coatings. Various products incorporating the alkoxy two-part cure system are used to protect surfaces and components exposed to plume radiation from various rocket motors and jet engines.

The addition cure system (No. 4) has characteristics which permit rapid heat-accelerated cure, tough physical properties, virtually nil shrinkage, and, due to the platinum catalyst, the best overall flame resistance. Applications include solar cell protection, particularly for satellites, and burn-through protection for the liners of solid rocket motors. The only negative characteristic of the addition cure system is its susceptibility to inhibition. Because the system contains parts-per-million levels of platinum catalyst, it can be readily "poisoned." Among the most common inhibitors are sulfur-containing organic rubbers and organo-tin compounds which are often used as plasticizers in plastics and also as catalysts for other silicone coatings.

There are other silicone elastomeric cure systems, and one of the most significant applications is to coat fiberglass blankets for fire resistance. Spark protection welding blankets are a common application for peroxide-cured silicone coatings. Since peroxide-cured silicones require higher temperature cures, their usefulness is constrained by the substrate upper temperature limits. Also, selectivity of the specific peroxide is critical to prevent poor cures due to the oxygen inhibition; characteristic of many peroxides.

Another novel silicone elastomer coating which has been developed is a combination cure involving the ultraviolet photoinitiation via free radical formation to provide cross-linking. This ultraviolet mechanism is often combined with a standard cure mechanism to provide a combination cure. This system provides quick surface cure followed by the slower room temperature cure of unexposed, shadowed areas to ultimately provide a fully cured conformal coating. Processes using the combination cure can be used to minimize the time and space required to hold the coated parts until cure is completed before downstream assemblies can take place.

Other cure systems have been developed for silicone elastomers, but they find limited use as coating materials and were generally developed for specific applications such as building sealants or glazing compounds.

The most common form for silicone coatings is a dispersion of the silicone in solvent. If the coating is based on a tough elastomeric silicone, the uncured elastomer base is most commonly described as a dispersion because it contains insoluble components such as high surface area fumed silica for reinforcement and often other solid components such as titanium dioxide pigments for coloration or reflectivity properties. The carrier solvent for these dispersions may include chlorinated hydrocarbons, fluorochlorohydrocarbons, and both aromatic and aliphatic hydrocarbons. The dispersions also often include blends of solvents to provide the proper combinations of flow, evaporation, and application ease. Among the most common solvents for silicone dispersions are 1,1,1-trichloroethane, VM&P naphthas, and xylene. Low-molecular-weight alcohols such as ethanol and isopropanol and ketones such as acetone are not suitable because silicones are generally incompatible with these lower-molecular-weight oxygen-containing solvents. Fluorosilicones require the use of such solvents as methyl ethyl ketone and methyl isobutyl ketone for adequate dispersing. Fluorosilicone-dimethyl copolymer-based silicones can be dispersed adequately in 1,1,1-trichloroethane for thin layer application.

True solutions can also be made if the silicone contains no insoluble components. For example, true solutions can be made for unfilled silicones or for silicones that are resin reinforced. These coatings have limited use, however, because the final cured elastomeric coating lacks the overall toughness of the filled materials.

Recent developments have resulted in silicone coatings which have not involved the use of solvents. Because of environmental concerns, the use of solvent carriers for dispersions and solutions has become less desirable. In particular, fluorochlorocarbons and chlorinated hydrocarbons, despite

their low toxicity and nonflammability, are being phased out because of Montreal Protocol Agreements. Similarly, hydrocarbon solvents are undesirable because of their flammability, toxicity, and environmental effects. Silicone-based conformal coatings have been developed without solvent carriers. However, thin layer applications are difficult unless the viscosity is low enough to permit proper coating. Unfortunately, the technology for high-strength, low-viscosity, 100% solids, silicone coating does not exist. The current products, therefore, when cured, are very low strength and do not provide coatings that are resistant to handling. Research is ongoing to develop water-based dispersions, but to date, the demonstrated physical properties, although higher than the 100% solids coatings, are significantly less than the current solvent-based silicone coatings.

Methods of Applications

The methods of applications for silicone coatings depend on the device being coated and the specific type of silicone being used. Dipping, spraying, and painting are the most common types of application. The thinnest coatings result from spraying of two solvent dispersion utilizing standard aerosol spray guns. Needless to say, experience involving aerosol spraying is critical for acceptable coatings. Among the variables to consider are the following: viscosity, solvent, percent solids, pot life, and cure system choices.

The most securely sealed surface layer is accomplished by dip coating. Again, variables including solvent, bath life, and cure systems must be optimized. Additionally, the evaporation of solvent during the dip processing needs to be compensated for by periodically or continuously adding make-up solvent to maintain optimal bath viscosity. If a one-part humidity-actuated cure system is used, consideration must be given to provide a dry blanket over the bath to prevent a partially cross-linked elastomeric skin from forming. Dry argon is often utilized to prevent moisture in the air from reacting with the silicone base coating. Another consideration for the dip coatings is the possibility of air bubble inclusion. Again, several variables need to be considered. Low viscosity, controlled immersion and withdrawal rates, and vibration of the bath and/or object to be coated can be used to minimize bubble entrapment. Similarly, the use of two distinct solvents with different rates of evaporation are often used to ensure uniform coating with minimal drip regions and minimal bubble formation.

Painting or brush coating substrates is yet another method to apply a uniform silicone coating. Painting, however, is usually not applicable for either large areas or mass production coatings. For painting application, virtually all of the variables discussed in the above dipping and spraying also apply.

Regardless of the methods of application, the cure parameters demand significant considerations. Vacuum exposure may be used to remove air bubbles and to ensure flow under surface irregularities or impregnation of porous substrates. Vacuum treatment may also be used to enhance removal of the solvents, but care should be taken to prevent evaporation of the reactive volatile components which would prevent cure even after removal from the vacuum. Of course, most commonly, the vacuum removal of solvent is unwarranted and therefore solvent is merely evaporated at ambient pressures. The solvent evaporation can also be enhanced by air circulation and by acceleration with heat. However, the application of heat should be limited or applied in a stepwise manner to prevent solvent entrapment below the surface resulting in solvent bubble formation. Also, for one-part silicone coatings which are cured via moisture activation, it is ineffective to use heat acceleration because humidity is obviously reduced in a normal air circulating oven. If accelerated cure is required for one-part coatings, a steam autoclave may be used, *but only after all of the carrier solvent is removed.*

TESTING CONDITIONS

The test requirements for silicone coatings include MIL-I-46058C for qualifying silicone coatings as insulating compounds for electrical coating applications of printed circuit board assemblies. MIL-I-46058C includes the following tests:

Curing Time and Temperature
Appearance
Coating Thickness
Fungus Resistance
Insulation Resistance
Dielectric Withstanding Voltage
Leakage Current Testing
Q Resonance
Q Resonance after Immersion
Thermal Shock
Flexibility
Thermal Humidity Aging
Flammability

Materials which are used in applications for spacecraft are tested via ASTM Test Method for Total Mass Loss and Collected Volatile Condensable Materials from Outgassing in a Vacuum Environment (E 595). This test is used to determine the amount of collected volatile condensable material and total mass loss that eludes from a material when exposed to 125°C for 24 h at vacuum less than 5×10^{-5} torr. Basically, the maximum CVCM value for coatings intended for space applications is 0.1% and the maximum TML is 1.0%. The coatings intended for satellite applications require these high levels of purity to prevent the contamination of solar cells, optical surfaces, and other sensitive instrumentation. For most silicone materials, extended devolatilization is required for the polymeric components prior to compounding into the finished product.

For silicone elastomeric coatings, the physical properties of the cured elastomer are critical parameters. The tensile strength, elongation, and modulus are defined in ASTM Test Methods for Rubber Properties in Tension (D 412). Durometer and tear strength measurements are defined in ASTM Test Method for Rubber Property—Durometer Hardness (D 2240) and ASTM Test Method for Tear Strength of a Convential Vulcanized Rubber and Thermoplastic Elastomer (D 624) respectively. The viscosity, nonvolatile content, and specific gravity tests are defined in ASTM Test Method for Viscosity of Adhesives (D 1084), ASTM Test Method for Weight Loss of Plasticizers on Heating (D 2288), and ASTM Test Method for Specific Gravity (Relative Density) and Density of Plastics by Displacement (D 792), respectively.

Other tests have been developed for silicone coatings to meet the requirements of specific applications. Included among these are the "blocking" test to determine the propensity of silicone coatings to cause "sticking" to contacted surfaces after application and cure. This test involves contact between the silicone-coated surface and the surface to be tested by subjecting the interface to an applied pressure for a fixed time followed by measurement of the force needed to reseparate the surfaces. A variety of tests have been developed to measure the adhesive force of the coating on the substrate. Again, a number of tests which are oriented toward the specific application have been developed and revised.

SPECIFIC APPLICATIONS FOR SILICONE COATINGS

Among the varied applications for silicone coatings is the conformal coating of electronic circuit boards. Because of their previously described stability properties, silicones make ideal conformal coatings. Silicone coatings typically have stiffening points of −65°C, and can be formulated with stiffening points as low as −115°C. This makes them ideal for extreme environment electronic device protection.

Silicone coatings are used almost exclusively to provide protection from atomic oxygen degradation in low earth orbit (approximately 100 to 500 miles high). Atomic oxygen degradation is significant enough to rapidly erode and degrade organic substrates including epoxies, urethanes, and polyester-based thermosets. Coating protection permits the use of composite materials in space applications where the advantages of high strength and low weight associated with composite materials would be unusable due to their atomic oxygen degradation.

The high-temperature stability and excellent dielectric properties of silicone resins make them ideal impregnant coatings for high-energy capacitors used in jet engine ignitions. The inherent stability of silicone coatings when combined with specific fillers including zinc oxide, titanium dioxide, and zinc orthotitanate are often used to provide specific emissivity and reflectance required for thermal control coatings. Similarly, silicone elastomeric coatings are produced by the addition of iron oxide, glass or ceramic microballoons, and graphite fibers, which provide ablation protection. Launch vehicles, launch equipment, and thrust reversers are often coated with specially formulated silicone ablative coatings. The incorporation of phenyl siloxanes into the basic silicone polymeric species provides increased ablative properties, and various copolymers—including silicone-boranes and silphenylenes—have and are being evaluated to provide protection from impingement of high-energy lasers.

As discussed previously, the biocompatibility of silicones makes them ideal for medical applications. Coating permanent implants as well as temporary implants with silicones provides improved safety and efficacy. Foley catheters coated with silicone elastomers result in less patient discomfort and reduced infection rates. For similar reasons, temporary pressure-sensitive silicone adhesive coatings are used to provide adhesion directly to the skin. Combinations of silicone coatings are being investigated for use in various drug delivery devices. Specifically layered coatings of silicones impregnated with drugs can be used for transdermal drug delivery. When combined with a silicone pressure sensitive adhesive, a complete system of controlled drug delivery devices can be fabricated.

NEW REQUIREMENTS FOR SILICONE COATINGS

Research and development efforts continue to provide silicone coatings with even more stringent requirements and specifications. Electrical coatings with semiconducting properties for electronic applications and elastomeric coatings with volume resistivities in the 10^{-4} to 10^{-5} ohm-centimetre range are being investigated. Silicone coatings with variable electric properties are also being researched.

Similarly, silicone coatings which provide specific biological properties are also being developed. Specifically, hydrophilic silicone coatings are being developed for reduced thrombogenicity, and microporous coatings are under development for controlled tissue in-growth response.

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Vinyl Resins for Coatings

by Richard J. Burns[1]

VINYL RESINS FOR COATINGS

Definition

THE VINYL RESINS USED IN solvent-based coatings, inks, and adhesives are low-to-medium molecular weight co- and tercopolymers of vinyl chloride, vinyl acetate, or other monomers to improve solubility. Functional monomers contribute specific properties; thus, carboxylic acid-containing monomers provide adhesion, while hydroxyl-containing monomers contribute to reactivity, compatibility with other resins and polymers, or adhesion to specific surfaces. These modified vinyl resins are most often used as thermoplastic, solvent-soluble lacquers, though by formulating with appropriate modifiers, air-dry or baking finishes can be produced having thermoset-like properties.

Special techniques have been developed that enable the use of high-molecular-weight vinyl chloride homopolymers as dispersions in organic media called plastisols or organosols that require a heat fusion step to form films or coatings. Vinyl chloride homopolymers and copolymers are also compounded for use as powder coatings for application by either electrostatic spray or fluidized bed techniques. Water-based vinyl chloride polymers and copolymers include high-molecular-weight polymer latexes that require heat to fuse, and also aqueous dispersions of low-molecular-weight polymers that utilize coalescents to form films at room temperature.

General

Important characteristic features of vinyl resins/coatings are: (1) relatively high glass transition temperature; (2) excellent resistance to water, alcohols, aliphatic hydrocarbons, vegetable oils, dilute acids, and alkali; and (3) inertness in contact with foods (FDA-listed resins only).

Vinyl resin films can be degraded by exposure to high temperatures or by long-term exposure to ultraviolet light, with a resultant change in color from clear to amber, red, and eventually black. Suitable heat stabilizers are employed that allow the processing of vinyl coatings at high temperature, while proper pigmentation helps to protect vinyl coatings from attack by UV light. Some stabilizer systems can provide limited protection to clear vinyl films.

[1]Union Carbide Corporation, Bound Brook, NJ 08805.

History

About 1912 Ostromislenski pioneered the industrial investigation of vinyl polymers and made and fractionated poly(vinyl chloride). E. W. Reid invented the copolymers of vinyl chloride and vinyl acetate in 1928. In 1933, Davidson and McClure described applications of vinyl resins including their use as swimming pool coatings [*1*].

Commercial production of poly(vinyl chloride-vinyl acetate) resins was begun in 1936. Carboxyl-modified copolymers were introduced in 1939 and hydroxyl-modified resins in 1945. The first commercial use of these vinyl resins was in 1936 as a coating for the inside of beer cans.

Organosol and plastisol coatings technology that permitted the use of very-high-molecular-weight resins were developed about 1943 [*2,3*].

Polymerization

Vinyl chloride monomer is a gas at standard conditions with a boiling point of −13.9°C. Polymerization is carried out in autoclaves under moderate to high pressure. The reaction is typically initiated by free radical generating compounds such as peroxides. The polymerization is exothermic, and reaction temperature regulation is necessary to control the growth (molecular weight) of the polymer. The use of high pressure and low temperature generally favors the formation of high-molecular-weight resins, and chain transfer agents are commonly used to control molecular growth. The number average molecular weight (M_n) of commercially available solvent-soluble vinyl chloride homopolymers and copolymers ranges from a low of a few thousand to about 45 000. The M_n of vinyl resins used for plastisol and organosol coatings ranges between about 60 to 110 000 [*4*].

Manufacture

Vinyl resins for coatings are made by several processes. Polymerization by solution and suspension processes is used to make the solvent-soluble resins, while emulsion or dispersion polymerization is used to make the much higher molecular weight polymers for plastisols and organosols. Some solvent-soluble grades are also made by the emulsion process. Post-polymerization processes are applied to some resins to achieve special properties.

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Solution Process

Polymerization is carried out in a solvent in a batch or continuous process. The viscosity of the reaction medium increases as monomer is converted to polymer, and the extent of polymerization can be monitored and controlled via viscometry. When the appropriate viscosity is attained, the autoclave varnish is stripped of unreacted vinyl chloride monomer, and the polymer is precipitated by the addition of water or water/alcohol mixtures; the slurry is centrifuged to remove most of the liquid, then the resin is dried in fluid-bed dryers. The particle size of the dried resins produced by this process ranges from about 75 to about 200 μm, and the particle shape is irregular.

Suspension Polymerization

Suspension polymerization is generally carried out in a water medium. High-molecular-weight water-soluble colloidal polymers are used in small amounts to stabilize the droplets of suspended monomer(s) to control particle size. The stabilizer used remains with the resin during and after polymerization and resin recovery. Normally the preparation of solutions of suspension resins requires that mild heating be employed to achieve maximum clarity of solutions at minimum viscosity. Particles of suspension vinyl resins are characterized as spherical with a size between 100 to 300 μm.

Emulsion Polymerization

Like the suspension process, emulsion polymerization is also carried out in water, but in place of water-soluble polymers, surfactants are normally used to stabilize the smaller monomer droplets during polymerization. A special form of emulsion polymerization called dispersion polymerization uses an oil-soluble rather than water-soluble initiator and produces resin of particles size ranging from about 0.2 to 2 μm. These high-molecular-weight powdered products are used in plastisol and organosol coatings.

Post-Polymerization Process

Some vinyl-alcohol modified resins are prepared in a two-step process. The first step consists of the preparation of a poly(vinyl chloride-acetate) copolymer by either a solution or suspension process. Next, the copolymer resin is dissolved in a suitable solvent and a catalyst is added to partially hydrolyze the pendant acetoxy groups to yield a vinyl alcohol moiety. The modified resin is then precipitated from solution and dried as described for the solution process. The resin thus formed has only secondary hydroxyl groups, which accounts for its unique solubility/compatibility properties.

These vinyl-alcohol-containing resins differ from those prepared directly using other hydroxy-containing monomers in their compatibility with alkyds and in the rate of reactivity with coreactants such as isocyanate or amino-formaldehyde cross-linkers.

Vinyl Chloride Copolymer Coating Resins

Four types of solvent-soluble coating resins offered by Union Carbide are shown in Table 1. These polymers are produced by the solution polymerization process.

1. Vinyl chloride-vinyl acetate copolymers.
2. Carboxyl-modified vinyl chloride-vinyl acetate copolymers.
3. Hydroxyl-modified copolymers of two types:
   a. Hydroxyalkyl acrylate modified directly polymerized.
   b. Vinyl-alcohol-modified polymer derived from poly(vinyl chloride-vinyl acetate) in a post-polymerization process.
4. Epoxy-modified vinyl chloride copolymers.

Other suppliers of solvent-soluble vinyl resins and their product lines are listed in Tables 2 through 5 for Denka Kagaku, BASF, Wacker Chemie, and Nissan.

FDA Status

Vinyl copolymer resins are listed by chemical identity in several U.S. Food and Drug Administration regulations such as 21CFR 175.300, 176.170, 176.180, and 177.1210 as components of coatings on metal and paper substrates for use as food contact surfaces of articles used in processing, manufacturing packing, producing, heating, packaging, holding, or transporting food, or as components of closures with sealing gaskets for food containers. Vinyl chloride-acetate copolymers, hydroxyl-modified vinyl chloride-acetate copolymer, and several other vinyl chloride copolymers made with monomers having acid or ester functionality are described.

Vinyl Resins—Analysis

There are many references to chemical methods for identifying and characterizing vinyl resins [*5,6*]. However, the infrared spectra of vinyl resins are very useful for qualitative and quantitative purposes. Spectra of neat vinyl resins can be found in sources such as atlases, encyclopedia of plastics, or specific papers dealing with the subject [*7–9*].

Also, several ASTM documents deal with the identification and characterization of vinyl resins used in coatings materials. ASTM Guide for Testing Poly(Vinyl Chloride) Resins (D 4368-89) describes methods for homo- and copolymer vinyl resins to determine important characteristics such as total chlorine content for composition, dilute solution viscometry to assess polymer molecular weight, high and low shear viscosity measurements to characterize vinyl dispersion resins for plastisols and organosols [*10*].

ASTM Test Method for Infrared Identification of Vehicle Solids from Solvent-Reducible Paints (D 2621-87) covers the qualitative characterization of separated paint vehicle solids by infrared spectroscopy. A spectrum for an ortho-phthalic alkyd, vinyl chloride-acetate modified vehicle is presented [*11*].

ASTM D 2124-70 (Reapproved 1988), Test Method for Analysis of Components in Poly(Vinyl Chloride) Compounds Using an Infrared Spectrophotometric Technique, presents methods whereby vinyl compounds can be separated into components including resins, plasticizers, stabilizers, and fillers. Each component can then be analyzed by infrared technique [*12*].

TABLE 1—Typical properties of UCAR® solution vinyl resins.

UCAR® Solution Vinyl	Polymer Composition, wt%			Reactive Functionality		Inherent Viscosity, ASTM D 1243	Glass Transition Temperature (T_g), °C	Average Molecular Wt, M_n*	Solution Viscosity[h] at 25°C, cP
	Poly(vinyl chloride)	Poly(vinyl acetate)	Other	Type	Wt%				
VYNS-3	90	10	...	...	...	0.74	79	44 000	1300[i]
VYHH	86	14	...	...	...	0.50	72	27 000	600
VYHD	86	14	...	...	...	0.40	72	22 000	200
VMCH	86	13	1[a]	Acid	1.0	0.50	74	27 000	650
VMCC	83	16	1[a]	Acid	1.0	0.38	72	19 000	100
VMCA	81	17	2[a]	Acid	2.0	0.32	70	15 000	55
VERR-40	82	9	9[b,c]	Epoxy	1.8[g,h]	...	67	15 000	...
VAGH	90	4	6[d]	Hydroxyl	2.3	0.53	79	27 000	1000
VAGD	90	4	6[d]	Hydroxyl	2.3	0.44	77	22 000	400
VAGF	81	4	15[e]	Hydroxyl	1.0[f,g]	0.56	70	33 000	930
VAGC	81	4	15[e]	Hydroxyl	1.9	0.44	65	24 000	275
VROH	81	4	15[e]	Hydroxyl	2.0	0.30	65	15 000	70
VYES-4	67	11	22[e]	Hydroxyl	3.0	0.15	54	5 500	20

*Referenced to polystyrene standard.
[a]Maleic acid.
[b]Epoxy-containing monomer.
[c]Solution—40% resin in MEK/toluene 3 × 2.
[d]Poly(vinylalcohol).
[e]Hydroxy alkyl acrylate.
[f]Oxirane oxygen.
[g]On solids.
[h]30% resin in MEK.
[i]20% resin in MEK.

TABLE 2—Solution vinyls from Denki Kagaku.

Grade	Composition, wt%				Inherent Viscosity
	Vinyl Chloride	Vinyl Acetate	Carboxylic Acid	Acrylic Ester	
1000A	86	14	...	...	0.5
1000AS	86	14	...	...	0.4
1000C	86	13	1	...	0.5
1000CS	86	13	1	...	0.4
1000GKT	91	3	...	6	0.5

TABLE 3—Suspension vinyls for solution coatings—BASF.

Grade	Composition, wt%		Approximate Solution Viscosity,[a] MPa·s
	Vinyl Chloride	Vinyl Isobutyl Ether	
MP-25	75	25	35
MP-35	75	25	35
MP-45	75	25	45
MP-60	75	25	60

[a]20% resin solutions in toluene.

Formulation of Solution Coatings

A typical vinyl coating usually consists of resin, solvent(s), plasticizer, pigments (required for exterior exposure), and optional ingredients such as stabilizers, modifying resin(s), and cross-linker(s).

The resin is normally selected on the basis of its ability to provide adhesion to the substrate. While, in most cases, strong adhesion is desired, there are special coatings such as strippable or peelable coatings where adhesion is not wanted. Table 6 lists the relative adhesion of several vinyl resins to various polymers and substrates.

The resin selection may be made on the need for reactive functionality to produce cross-linked coatings that change the nature of the coating from thermoplastic to thermoset-like properties that are characterized by improved solvent or stain resistance.

Solubility

Variation in the ratio of vinyl chloride to vinyl ester and the degree of polymerization produce a wide range of vinyl polymers with different solubility characteristics. Highest solubility is favored by low vinyl chloride content and low molecular weight. This relationship in terms of viscosity of resin solutions is compared in Table 1.

TABLE 4—Suspension vinyls for solution coatings—Wacker Chemie.

Grade	Composition, wt%				Inherent Viscosity
	Vinyl Chloride	Vinyl Acetate	Acid	Acrylic Ester	
E 15/45	85	15	...	...	0.5
H 15/45	85	15	...	...	0.5
H 15/50	85	15	...	...	0.6
H 40/43	60	40	...	...	0.46
H 40/50	60	40	...	...	0.6
H 40/55	60	40	...	...	0.7
H 40/60	60	40	...	...	0.88
E 15/45M	84	15	1	...	0.5
H 15/45M	82	17	1	...	0.56
E 15/40A	85	...	...	15	0.4
E 20/55A	80	...	...	20	0.68
E 22/48A	78	7	...	15	0.56

TABLE 5—Suspension vinyls for solution coatings—Nissan.

Grade	Composition, wt%			
	Vinyl Chloride	Vinyl Acetate	Vinyl Alcohol	Acid
MPR-TA	91	3	6	...
MPR-TS	87	13	...	...
MPR-TM	86	13	...	1

Vinyl solution resins are dissolved by ketones, esters, certain chlorinated solvents, and some nitroparaffins. As a class, ketones are the best solvents in terms of the ability to dissolve higher solids at lower solution viscosity. Hydrocarbons are chiefly used as diluents primarily to lower cost. Aromatic and aliphatic hydrocarbons can be usd as diluents. Aromatic hydrocarbons, chiefly toluene and xylene and higher boiling fractions such as Aromatic 100 or 150, are preferred as they can be used at high levels, in the range of 50 to 65% of the solvent blend depending on the resin composition, molecular weight, and desired solids. The Aromatic 100 and 150 are usually used only in baking finishes.

Aliphatic hydrocarbons can be used in limited amounts, up to about 30% of the solvent blend. Higher levels can lead to viscosity instability, and only low boiling aliphatic hydrocarbons, those with boiling points up to 117°C, are suitable. The use of higher boiling aliphatic hydrocarbons can cause precipitation of the resin during drying.

Alcohols are strong precipitants for vinyls and are not generally used in unmodified vinyl lacquers. However, in some cases vinyls, usually hydroxyl-modified vinyls, are readily formulated with other resins that are carried in alcohol. With these, up to 15 to 20% alcohol may be used in the solvent blend. Careful attention must be paid in vinyl coating formulations that contain alcohols to be sure that problems do not develop during application and drying of the coatings. Glycol ethers and glycol ether esters are sometimes used in vinyl coatings to improve flowout of baked coatings.

In response to regulations restricting the type and amount of solvents used in coatings, such as Los Angeles Rule 66 and later versions, vinyl coatings were reformulated as compliant systems by reducing the amount of branched ketones and aromatic hydrocarbons and making up the difference with esters and aliphatic hydrocarbons [*13*]. Though it was necessary to use more oxygenated solvents, the performance of compliant coatings stayed the same. Typical solvent blends used for spray application and the reformulated compliant systems are shown in Table 7.

Solution Characteristics

From the time a vinyl resin is dissolved, the viscosity of solutions increases with time until an equilibrium is reached after which the viscosity remains constant. This behavior is believed due to the formation of regions of microcrystallinity between polymer molecules in solution. The extent of the viscosity increase is dependent on: (a) resin molecular weight; (b) solids content of the solution; (c) and the strength of the solvent blend. The viscosity increase may be small or so large that the solution sets to a gel. Properly formulated vinyl resin solutions usually reach an equilibrium viscosity in about 3 to 5 weeks. Guidelines for the preparation of viscosity stable solutions for resins of varying molecular weight are shown in Table 8.

Vinyl chloride copolymer solutions also exhibit what is known as the memory effect. When a vinyl resin solution is heated to about 60°C, the effect of microcrystallinity is eliminated. If the solution is then cooled to its original temperature, the viscosity will not immediately return to its original value because of the time lag needed for the effect of the microcrystallinity to redevelop. With time, the viscosity of the solution will return to the same value as that of a solution that was not heated. The converse relationship hold when vinyl solutions are cooled. A graphical presentation of the memory effect is presented in Fig. 1.

Plasticizers

Plasticizers are often used with vinyl resin coatings to improve flexibility, formability, and impact resistance of the coating. Monomeric as well as polymeric plasticizers or compatible polymers with low glass transition temperature (T_g) may be used to plasticize a vinyl coating.

TABLE 6—Adhesion of vinyl resins.

Substrate	Product Type: Copolymer VYHH	Carboxy Modified VMCH	Hydroxy Modified VAGH VAGF	WB Vinyl AW-875
Steel	0	10	5	0
Galvanized	0	10	5	0
Paper (glassine)	10	10	10	10
Aluminum foil	0	10	7	10
Polyethylene, treated	0	0	0	0
Polypropylene, treated	0	0	0	0
Polysulfone	7	10	10	10
Acrylic	10	10	10	10
PVC plastic	10	10	10	10
ABS plastic	10	10	10	10
Polycarbonate	10	10	10	10
Polyphenylene oxide	4	10	0	0
Polyethylene terephtalate	0	0	5	0
Impact polystryene	0	0	0	0
Inked surface	0	5	8–10	5

Rating: 10 = Pass Scotch Tape Test, no loss of adhesion.
5 = Some loss of adhesion, not recommended.
0 = No adhesion.

TABLE 7—Typical solvent mix for spray-applied coatings, composition, wt%.

Non-Regulated		Rule 66 Compliant		Compliant with Rule 66/EPA 33/50 Initiative[a]	
MIBK	50	MEK	14	MEK	7
Toluene or Xylene	50	Butyl acetate	46	Acetone	3
	100%	Cyclohexanone	9	MIAK	15
		Toluene	12	Butyl acetate	40
		Xylene	7	Cyclohexanone	9
		VM&P naphtha	12	Toluene	6
			100	VM&P naphtha	20

[a]50% reduction of MEK and toluene, which are EPA 33/50 listed solvents.

TABLE 8—Guidelines for viscosity stable solution.

Resin Molecular Weight × 10^{-3}	Resin	Maximum Solids	Typical Solvent Blend, wt%
44	VYNS-3	15	MEK/toluene, 67/33
27–34	VAGF, VAGH, VMCH, VYHH	25	MIBK/toluene, 50/50
19–22	VAGC, VAGD, VMCC, VYHD	28	MIBK/toluene, 50/50
15	VERR, VMCA, VROH	33	MIBK/toluene, 33/67
5.5	VYES-4	60	MEK/toluene, 10/90

Phthalate, phosphate, and glycol ester plasticizers are typically used. Plasticizers are selected to meet the requirements of the coating that may include low-temperature flexibility, resistance to extraction by solvents, resistance to migration, to humidity, etc. Blends of plasticizers may be required to meet specific requirements. Table 9 presents a listing of plasticizers that are commonly used with vinyl resins. Care must be exercised in choosing the level of plasticizer as excessive amounts tend to make the film soft and prone to dirt retention. Ordinarily, a level of 25 phr (parts per hundred parts resin) of plasticizer is considered about maximum for use with coating resins.

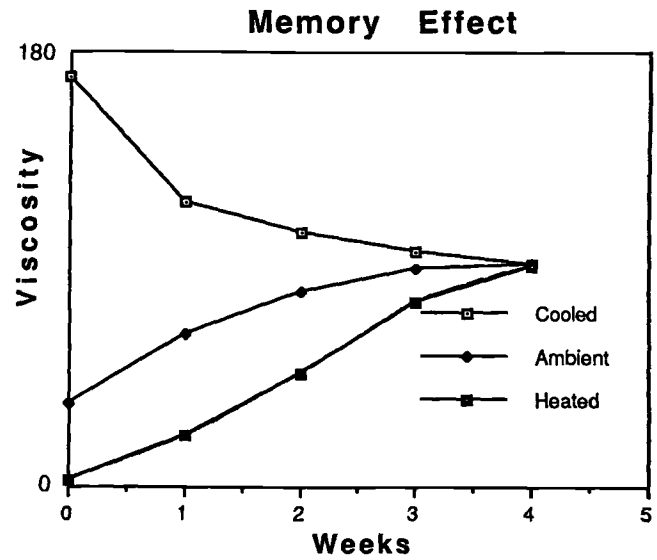

FIG. 1–Memory effect.

Pigmentation

Vinyl coatings are pigmented (1) to achieve the desired color, and (2) to prevent degradation of the vinyl resin from the effect of ultraviolet light for coatings that are intended for use outdoors [*14*]. Most organic and inorganic pigments can be used. However, basic pigments must be avoided with carboxyl-modified resins, as these pigments can react to form irreversible gel.

Prime or color pigments which absorb UV radiation must be used at a level sufficient to protect the vinyl resin. Extender pigments or fillers do not absorb UV radiation and can only be used in combination with a UV absorbing pigment. For titanium dioxide (T_iO_2) pigments, a minimum level of about 75 phr is needed to provide resistance to UV light. Other inorganic pigments can be used to replace T_iO_2 by substituting on an equal volume basis. Organic pigments that are

TABLE 9—Typical plasticizers compatible with solution vinyls.

Phthalates	Linear Dibasic Acid Esters
Butyl benzyl phthalzate (BBP)	Di-*n*-butyl sebacate (DBS)
Di-2-ethylhexyl phthalate (DOP)	Di-2-ethylhexyl adipate (DOA)
Diisooctyl phthalate (DIOP)	Diisononyl adipate (DINA)
Diisononyl phthalate (DINP)	Di-2-ethylhexyl azelate (DOZ)
Diisodecyl phthalate (DIDP)	
	Phosphates
Citrates	
	Tri-2-ethylhexyl phosphate (TOP)
Acetyl tri-*n*-butyl citrate	Isodecyl diphenyl phosphate
Epoxies	Polymerics
Epoxidized soybean oil (ESO)	Adipic acid polyesters
2-Ethylhexyl epoxytallate	Azelaic acid polyesters

manufactured to smaller particle size are used at a lower concentration, and blends of inorganic and organic pigments are often used to achieve the desired color. Excessive high loading of pigments can lead to early chalking.

Organosols and Plastisols

A plastisol is a dispersion of discreet particles of high-molecular-weight vinyl homopolymer resin in plasticizer, with a low level of heat stabilizers sufficient to prevent degradation during baking (fusing). Plastisols normally require a minimum amount of about 55 to 60 parts plasticizer per hundred parts of resin to form a fluid mix. The viscosity of the dispersion is dependent on packing effects, the volume of dispersed resin relative to the volume of liquid plasticizer, the size and shape of the suspended particles, solvating or swelling effect of the plasticizer on the resin particles, and the viscosity of the liquid plasticizer. The relatively high levels of plasticizer needed to produce a flowable liquid mix results in the formation of fused films too soft for use as coatings. Plastisol coatings are usually formulated with the addition of coarser particle-size PVC resins called extenders from suspension or bulk (mass) polymerization that allow the use of less plasticizer and thus harder films. Additionally, small amounts of thinner, usually aliphatic hydrocarbon, are used (up to about 10 wt%) to reduce viscosity and provide better flow and leveling of the plastisol coating. Plastisol coatings do not adhere well to most substrates and most often require the use of a suitable primer.

An organosol differs from a plastisol in that much lower levels of plasticizer are used. A combination of weak solvents called dispersants in combination with hydrocarbon solvents called diluents are used to provide sufficient fluid to make a fluid dispersion. Because lower levels of plasticizer are used, films with much greater hardness can be obtained.

Commercial organosols are usually modified with a solvent-soluble resin to prevent mud cracking or film splitting during the bake to fuse the film. The modifier resin may contain carboxyl groups to make self-adherent coatings, or it may be a hydroxyl containing resin to provide functionality to react with cross-linkers such as amino or phenol/formaldehyde resins to achieve a degree of thermoset properties. Though vinyl copolymers are usually the modifier of choice for organosols, other polymers such as acrylic polymers may be used.

Careful consideration must be given to the selection of the solvent/diluent mix for organosols to attain the highest solids coupled with good viscosity stability. Commercial organosols of 50 to 55% nonvolatile by weight are typical.

Plastisols and organosols require a high baking temperature of about 350°F (177°C) to fuse the films. At elevated temperature, the plasticizer or plasticizer diluent mix exerts a strong solvating or swelling effect on the dispersed PVC resin particles. At fusion, the resin no longer exists as discreet particles, but rather as a continuous, homogeneous film. Films of plastisols or organosols need only to reach fusion temperature and do not have to be held at the fusion temperature for a long time period. Undercuring or baking at temperatures lower than that required for fusion will yield films deficient in tensile strength, elongation, abrasion resistance, and all other properties.

Plastisols and organosols also require the use of heat stabilizers to protect the vinyl resin against degradation during the fusion bake. Heat stabilizers are usually combinations of metal salts of organic acids in combination with epoxidized oils or liquid epoxy resins. Special attention must be given to the selection of heat stabilizers for organosols modified with solvent-soluble resin, especially when carboxyl-modified polymers are used. In such cases, the metallic salts must be avoided as these will usually cause gellation; typically, mercapto tin or tin ester compounds are used in combination with an epoxy stabilizer.

The type of pigment and level of pigment used in pigmented organosols follow the guidelines given for solution vinyl resins.

It is, however, more difficult to prepare pigmented plastisols because there is generally little solvent used to control viscosity. Low oil absorption pigments must be used to avoid excessively high viscosity.

Primers for Plastisols and Organosols

Plastisol coatings need a primer to develop good adhesion to metal substrates. An organosol coating may also require a primer if it is not modified with an adhesion-promoting modifier. Suitable primers can be formulated from carboxyl-modified vinyl resins and may require the use of thermoset resins such as amino-formaldehyde or phenolic resins to provide

resistance to excessive softening from highly plasticized plastisol or organosol coatings.

MAJOR MARKET AREAS FOR VINYL COATINGS

Rigid Packaging

Liners for Interior Surface Coatings, Cans, Can Ends, Closure/Caps and Crowns

The first commercial use for vinyl coatings was as the topcoat lacquer for the inside of beer cans. As beverage cans evolved from three- to two-piece construction, the vinyl coating also changed from lacquer to hydroxy vinyl/amino-formaldehyde thermosets to meet the need for higher corrosion resistance. Thermoset coatings of epoxy-modified vinyl resin with carboxyl-modified vinyl resin are used to coat on coil stock. The coated coil stock is then formed into the stay-on tab can ends, an application that requires excellent mechanical properties to withstand the forming steps without cracking.

Organosol coatings containing a solution resin component, usually carboxyl-type for adhesion, have also been used on precoated stock for can ends. Vinyl organosols are further modified with amino-formaldehyde or phenolic resins to upgrade chemical resistance and permit the use of such coatings for packaging food that will be autoclaved to sterilize the contents [*15*].

Vinyl lacquer and vinyl thermoset coatings are used as size coats for metals that are formed in caps and closures for jars or as crowns for beverage bottles. These systems serve as the primer coat for gasketing compounds made with plastisol or vinyl resin dry blends.

Flexible Packaging

Solvent-soluble carboxyl-modified vinyl chloride copolymers have good adhesion to most materials used in flexible or semi-rigid packaging including aluminum foil, paper and plastic films such as polyethylene terephthalate, polycarbonate, PVC, and cellophane. This type of resin is used for its adhesion characteristic, ease of heat sealing, and resistance to attack by the packaged product. The vinyl resin may be used alone or modified with plasticizers or other resins and polymers to formulate heat-sealable coatings for applications requiring varying degrees of force needed to open the container. This could range from applications such as blister packaging where the bond needs to be strong enough to cause substrate failure when the package is opened, to items such as jellies or cream containers found in restaurants where a tight but readily peelable bond is required.

Vinyl coatings are also used to coat collapsible metal tubes for packaging materials such as pharmaceutical preparations, toothpastes, and the like where the need is for a very flexible coating that will not crack nor be attacked by the contents of the package even though high stresses from collapsing and rolling up the tube are encountered.

Other applications include decorative coatings for the aluminum foil paper laminates for cigarette packaging, food wrappers for fast food restaurant items, for butter, margarine, soups, and so on. Decorative foil for floral wrappings, decorative labels, and coatings for aluminum foil for the vapor barrier insulation for construction applications are also coated with vinyl resin coatings.

Inks

The major markets for vinyl inks are on vinyl surface products such as floor and wall coverings, swimming pool liners, vinyl upholstery, and garment fabrics. Ink formulation is quite similar to that used with coatings except solvent choices are somewhat narrowed and higher pigment loadings are needed to achieve hiding in the thin films typical of inks.

Vinyl inks are often reverse printed on a clear vinyl film, and the printed film is then laminated to substrates such as wood or metal to make articles having simulated wood finish.

Vinyl inks are printed by gravure or screen process because these presses are compatible with the strong solvents needed for vinyls; flexographic printing is not suitable for vinyls because the plates are susceptible to solvent attack. Inks for highly plasticized vinyl surfaces are usually formulated with ester solvents to avoid excessive softening of calendered films and puckering of the films.

Dry Film Printing (Hot Stamp Transfer)

In this application, vinyl inks are printed on a carrier sheet such as polyethylene terephthalate, polyethylene, polypropylene, or other suitable surfaces to which the ink will not adhere strongly. The inks are applied and dried usually in web form. When ready for use, the printed carrier film is placed with the inked side on the surface to be decorated. A heated die presses the composite to make intimate contact with the surface, so that when the die is removed, the ink is firmly bonded to the substrate and the carrier is peeled away cleanly.

Maintenance and Marine Finishes

Heavy duty marine finishes were developed in the mid-1940s. These systems consisted of a poly(vinyl butyral) wash primer, vinyl-red lead anticorrosive intermediate coatings [based on poly(vinyl alcohol)-modified resin needed for adhesion to wash primer], and vinyl copolymer/wood rosin/cuprous oxide anti-foul top coats. This system has become the subject of numerous specifications; many U.S. Government agencies and agencies of other governments have written specifications with this coating system specified for use below the waterline of ships.

Because of their good water resistance, good weathering qualities, flexibility, fast dry and ease of application, and repair, vinyls quickly became established as maintenance finishes. This area includes coatings for locks, dams, appurtenant structures for waterways, interior linings for potable water tanks, steel structures such as bridges, electrical towers, equipment in chemical plants, and the like. Many specifications have been written that require the use of vinyls as maintenance paints [*16,17*].

The early vinyl maintenance and marine finishes were applied by air atomizing spray guns at low solids. Several coats were needed to attain coverage sufficient for good corrosion

protection. High-build airless spray-applied vinyl coatings were developed in the 1970s to fill the need for coatings systems that could be applied in fewer coats at less expense [*18*].

Wood Finishes

Reactive heavy duty vinyl finishes for wood have been developed consisting of a hydroxyl-modified vinyl resin cross-linked with amino/formaldehyde resins. Alkyd resins were often added to improve film build. Such finishes became established as the standard for kitchen cabinets because of their retention of excellent adhesion and water resistance, particularly when the coated wood becomes wet from high humidity or water splashing. These finishes also have excellent resistance to a variety of household chemicals, solvents, and stains and have been used as fine furniture finishes [*19*].

Magnetic Recording Media

Vinyls, especially hydroxy-modified vinyls, have been used as binders for magnetic iron oxide tapes since the beginning of the development of tape recording. The vinyl resins are used because of their good adhesion, abrasion resistance, and good pigment wetting properties. The early binder formulations used alkyd resin as plasticizers, then polyesters; currently, polyurethane resins are used as the plasticizer as the technology of tapes advanced and placed more stringent requirements on the performance of magnetic tape for audio and video [*20*].

Powder Coatings

Vinyl powder coatings are formulated with vinyl chloride homopolymers and copolymers for application by fluidized bed, powder spray, or electrostatic powder spray. Powder coatings are prepared by dry compounding resins, plasticizer, pigments, and additives in ribbon blenders followed by attrition or dispersion to powder in mixers such as the Henschel mixer. Some powder coatings are prepared by a melt mix technique followed by cryogenic grinding. This latter technique produces powders of smaller particle size [*21*].

Powder coatings prepared by dry compounding are usually applied by fluidized bed or by spray techniques. The metal parts are heated for fluid bed application so that the powder will adhere to the part and begin to flow to form a film. A bake after the powder application is needed to complete the film-forming process by fusion or melting.

Cryogenically ground powder coatings are applied by electrostatic powder spray. With the electrostatic method, it is not necessary to preheat the parts, but a bake is necessary after application to fuse the powder to a film. The finer particle size allows the deposition of smoother and thinner films than is attainable from fluidized bed or powder spray process. However, the high costs of cryogenic grinding made these materials substantially more expensive than dry grinding and as a consequence, the cryogenic ground powders account for only a small share of the PVC powder-coating market.

PVC powder coatings are used to coat products such as pipe, fencing, and metal furniture.

PVC Latex

Emulsion polymerized vinyl chloride homopolymers and copolymers are used in the latex form not so much to make finished coatings but rather as material coated on a base or support to provide the substrate for items such as wall coverings, backing for carpeting, and the like. In a sense, such use could be considered analogous to a waterborne version of an organosol coating. The vinyl chloride homopolymers need to be modified with a substantial loading of plasticizer, and some grades are sold as preplasticized latexes. These water-based materials require a high temperature bake to fuse the resin plasticizer mix into a continuous film.

By varying the type and amount of comonomer used to make emulsion polymerized copolymer latexes, lower T_g products are available that can use lower temperature bakes to form films.

Waterborne Vinyl Dispersions

Waterborne vinyl dispersions made from solution-polymerized vinyl copolymers became available in the 1980s. These waterborne vinyl dispersions are of medium molecular weight and have high T_g, about 80°C. Coalescents are needed with these products to form a film. Some dispersions are available with a glycol ether coalescent already present in the product, and a co-solvent free variety is also available. With the latter, the formulator can choose whichever coalescent, glycol-ether, glycol-ether ester, plasticizer, or blend of coalescents that best meets performance requirements. A line of waterborne vinyl dispersions is shown in Table 10.

Waterborne vinyl dispersions are used in many ink, coating, and heat-sealable coating applications where solvent-based vinyl coatings had been used.

Trends in Vinyl Coatings

To meet the VOC requirements that are either in place or proposed for the future, developments in vinyl coatings have centered on high solids and waterborne systems.

For high solids vinyl coatings, substantially increased resin solubility was achieved by reduction in the polymer molecular weight, so that viscosity stable solutions could be prepared at two to three times the level of solids content that was possible with earlier vinyl resins. However, at the low molecular weights needed for high solubility, the performance of coatings made from such resins was greatly reduced in terms of chemical resistance and physical properties. As a result, high solids vinyl resins are modified to contain hydroxyl functionality to allow for reaction with added coreactant materials to build molecular weight. Though the high solids resins may be used alone for less demanding applications, they are

TABLE 10—A line of waterborne vinyl resins dispersions.

	Composition, wt%			
Grade	Solids	Water[a]	Cosolvent[b]	pH
AW-850	38	50	12	7.0
AW-875	39	61	···	7.0

[a]Contains less than 2% amines.
[b]Ethylene glycol monobutyl ether.

best used either as a reactive system, with amino-formaldehyde or isocyanate cross-linker, or as modifiers for alkyds, polyester-isocyanate, or epoxy-amine coatings to improve initial drying or set-to-touch rate, or to improve recoatability [*21*].

The waterborne vinyl dispersions previously described represent an alternative to high solids vinyls as a way to formulate low VOC coatings. The waterborne vinyls are compatible with a wide variety of other waterborne resins with low VOC content such as acrylics, alkyds, urethanes, and amino-formaldehyde cross-linkers.

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16

Miscellaneous Materials and Coatings

by Joseph V. Koleske[1]

THIS CHAPTER IS CONCERNED WITH A VARIETY of products that are not discussed elsewhere in the manual. Some topics are mentioned only briefly to indicate that the area has not been forgotten and that the topic is not within the scope of the manual.

POLYOLS

Polyols, or polyalcohols as they are sometimes known, are compounds containing one or more, but usually two or more, free hydroxyl groups. Most definitions, and particularly those over ten years old, list typical polyols as compounds such as ethylene glycol, propylene glycol, neopentyl glycol, glycerol or glycerin, trimethylolpropane, pentaerythritol, and sorbitol that were used in the preparation of alkyds and polyesters. Today the word "polyols" is far more encompassing and more often than not refers to alkylene oxide [*1*] and ϵ-caprolactone [*2*] adducts of the above-mentioned and other monohydric or polyhydric alcohols, low-molecular-weight polyesters prepared from the above mentioned as well as other polyhydroxyl compounds and dicarboxylic acids (particularly adipic acid) [*3–5*], polytetrahydrofurans prepared by a cationic ring-opening polymerization of tetrahydrofuran [*6,7*], and low-molecular-weight polycarbonates [*8–10*]. There are other compounds that meet the above definition, but they are not usually termed polyols. Compounds such as these are certain vinyl chloride copolymers, hydroxyl-containing glycidyl ether compounds, vinyl alcohol copolymers, and so on. This chapter will not be concerned with these latter compounds since they are dealt with elsewhere in the manual.

Polyols are important compounds used in the manufacture of alkyds and polyurethane coatings, of intermediates used in radiation curable formulations, as copolymerizable ingredients in high solids and cationic photocure systems, as well as in a number of other end uses including elastomeric fibers, dentistry, artifact preservation, and pharmaceutical preparations. The two main classes of polyols used in coatings are the polyether polyols, which are typified by the poly(propylene oxide) polyols (PPO), and the polyester polyols, which include both poly(glycol adipates) (PEA) and poly-ϵ-caprolactone polyols (PCP). Both classes of polyols are available as difunctional and

$$HO—[CH(CH_3)—CH_2]_a—O—R—O—[CH_2—CH(CH_3)]_b—OH$$

Poly(propylene oxide) Polyol

$$H—[O(CH_2)_4O—CO(CH_2)_4CO]_u—O(CH_2)_4O—[CO(CH_2)_4CO—O(CH_2)_4O]_v—H$$

Poly(1,4-butanediol adipate) Polyester Polyol

$$H—[O(CH_2)_5CO]_s—O—R'—O—[CO(CH_2)_5O]_t—H$$

Poly-ϵ-caprolactone Polyol

trifunctional hydroxyl compounds though the adipates are almost always difunctional in nature. Higher functional polyols are known and available, but their usage is less common than that of the di- and trifunctional products. In the above structural formulas, R and R′ may be the same or different and —O—R—O— and —O—R′—O— are the residues of the polyhydric alcohol initiators.

Difunctional and trifunctional PPOs are usually initiated with 1,2-propylene glycol and glycerol, respectively. The adipate polyols are usually prepared with an excess of diol, so most end groups are hydroxylic rather than carboxylic in nature. Since these polyols are prepared by a condensation reaction, there is no need for an initiator. Caprolactone polyols are initiated with a variety of diols and triols such as diethylene glycol, ethylene glycol, 1,4-butanediol, trimethylol propane, glycerol, etc. The above structure for PPO indicates that the hydroxyl groups are both secondary, which is the usual case. However, from time to time a primary hydroxyl group will be found due to an unexpected opening of the propagating 1,2-epoxide. The subscripts *a*, *b*, *u*, *v*, *s*, and *t* in the above structural formulas can be the same or different, and they can take on a wide variety of values with the number average molecular weight ranging from about 150 to 3000 for polyols usually used in coatings. Details about preparation of urethane coatings based on polycaprolactone polyols for rigid substrates [*11*] and flexible substrates [*12*] are available.

A variety of other specialty polyols also exist such as poly(butylene oxide) and polybutadiene polyols, which are useful when very high levels of barrier hydrophobicity are needed [*13*]. Poly(tetramethylene oxide) polyols also have good hydrophobic character. New polyols are also being developed, including polyols based on lactose that have flame-retardant characteristics as well as polyols with different end capping, etc. [*14*]. Although new polyols such as these are often designed for use in the manufacture of polyurethane foams and elastomers, they can be and are used in coating formulations.

[1]Senior consultant, Consolidated Research, Inc., 1513 Brentwood Road, Charleston, WV 25314-2307.

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End capping polyols can provide adducts with different properties. For example, poly(propylene oxide) polyols which contain terminal secondary hydroxyl groups can be end capped with ethylene oxide to provide polyols with more reactive primary hydroxyl groups [*1,7*]. Ways to apply nuclear magnetic resonance to measure the ethylene oxide content of these and other propylene oxide/ethylene oxide copolymers is detailed in ASTM Test Methods of Polyurethane Raw Materials: Determination of the Polymerized Ethylene Oxide Content of Polyether Polyols (D 4875). Also described in the literature [*1,7*] are polyols modified to have amine, allyl, carboxyl, cyano, and vinyl ether end groups. Glycols that are solid and/or that have subliming characteristics, as 2,2'-dimethyl-3-hydroxypropyl 2,2'dimethyl-3-hydroxypropionate, can be modified with a few ethylene or propylene oxide groups to yield new polyols that are liquid, have low viscosity, and do not sublime with even a few molecules of ethylene oxide having nil or very little effect on moisture resistance [*15*]. Polyols can be end capped with an anhydride to form adducts that have free carboxylic acid functionality or a mixture of it and hydroxyl functionality as has been done with the poly-ε-caprolactone polyols [*16*] or the alkylene oxide capped glycols [*17*]. In other instances, poly(propylene oxide) polyols have had carboxyl groups grafted to their backbone with acrylic or methacrylic acid. These grafted polyols retain their original hydroxyl end groups and are used in coating formulations [*18*].

Polyols can be incorporated into alkyds, made into moisture-curing urethanes, can be cross linked with aminoplasts, and can be cross linked with cycloaliphatic epoxides when terminated with carboxylic acid end groups. In using the polyols, the hydroxyl number [*19*] is their most important physical characteristic to be measured and used. Five wet chemical methods and two nuclear magnetic resonance methods for determining the hydroxyl number are given in ASTM Method for Testing Polyurethane Polyol Raw Materials: Determination of Hydroxyl Numbers of Polyols (D 4274) and in ASTM Method for Testing Polyurethane Raw Materials: Determination of Primary Hydroxyl Contents of Polyether Polyols (D 4273), respectively. The equivalent weight or combining weight of a polyol is determined from the hydroxyl number by the following relationship

$$\text{Equivalent Weight} = 56\ 100/\text{Hydroxyl Number}$$

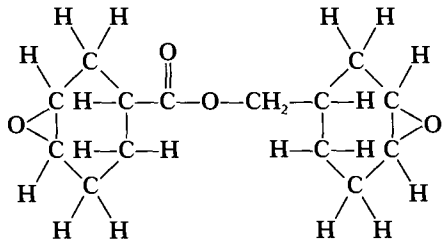
when potassium hydroxide is used as the titrating agent. Of course, if functionality is known, polyol molecular weight can be calculated by multiplying the equivalent weight by the functionality. Manufacturers provide information about hydroxyl number and usually about methods for analytically determining it.

Another important reactivity parameter is the acid number described in ASTM Test Method for Polyurethane Raw Materials: Determination of Acid and Alkalinity Numbers of Polyols (D 4662). Acidity and alkalinity in polyols can affect reactivity, shelf life, color, and hydrolytic stability of coatings prepared from polyols. Polyethers and poly-ε-caprolactone polyols usually have very low acid numbers. However, due to the nature of the condensation reaction coupled with transesterification used to produce polyester polyols, these polyols have relatively high acid numbers. Color, which has obvious implications, can be determined with ASTM Test Method for Polyurethane Raw Materials: Determination of Gardner and APHA Color of Polyols (D 4890).

CYCLOALIPHATIC EPOXIDES

Although the topic of epoxides in coatings is the subject of a separate chapter in this manual, that chapter deals with glycidyl or 1,2-epoxides that are not attached to a ring structure. Such epoxides are the largest volume products of all epoxides used, and the main products in this class are the diglycidyl ethers of bisphenol A. However, there is a special class of epoxides, termed "cycloaliphatic epoxides," that are used in specialty coatings and in cationic radiation-cure coatings. These epoxides are characterized by a saturated ring structure that imparts a high degree of weatherability and excellent electrical properties such as dielectric constant, dissipation factor, dielectric breakdown voltage, etc., to coatings and other products made from them. The good weatherability of the cycloaliphatic epoxides is apparent from the fact that they have been used for decades to make the large electrical insulators used in substations [*20*]. These compounds react well with carboxylic acids, as evidenced by their time-honored use as acid scavengers, and this reactivity often forms the basis for their use in coating formulations.

The main commercial cycloaliphatic epoxide is 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate that has the structure



This epoxide is well known by the familiar name designation ERL-4221. Table 1 contains the properties of this epoxide and other cycloaliphatic epoxides that are commonly known in the industry. Epoxide equivalent weight can be determined with ASTM Test Methods for Epoxy Content of Epoxy Resins (D 1652). Manufacturers can also be helpful in supplying information about methods of analysis for specific products. Usually these epoxides are reacted with polyols that function as flexibilizing agents for the highly cross-linked polymeric network that results. These epoxides polymerize by nucleophilic attack on the epoxide ring to form an ether linkage and a hydroxyl group on the ring. The hydroxyl group that is formed on the ring is quite acidic in character and will readily open other cycloaliphatic epoxide groups.

In the coatings industry, cycloaliphatic epoxides are used as a major formulating ingredient in cationic, photocurable formulations [*22*]. Usually they are formulated with polyols, onium-salt photoinitiators, and other ingredients. The onium salts photolyze in the presence of ultraviolet light to form strong protic acids that cause rapid polymerization of the epoxides as well as their copolymerization with active hydrogen compounds such as polyols. The presence of alkalinity including even very weak bases can result in neutralization of the protic acids formed by photolysis. Since the protic acids

TABLE 1—Commercial cycloaliphatic epoxides and their physical properties [*20,21*].

Chemical Name	Viscosity, cP at 25°C	Specific Gravity, 25/25°C	Color, 1933 Gardner (max)	Epoxide Equivalent Weight	Boiling Point, °C (mm Hg)	Vapor Pressure at 20°C, mm Hg	Solidification or Glass Point, °C
3,4-Epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate	350–450	1.175	1	131–143	354 (760)	<0.1	−20
Bis(3,4-epoxycyclohexylmethyl) adipate	550–750	1.15	1	190–210	258 (10)	<0.1	9
2-(3,4-Epoxycyclohexyl-5,5-spiro-3,4-epoxy)cyclohexane-m-dioxane	7000–17 000 at 38°C	1.18	2	133–154	>250 (760)	<0.01	<0
1-Vinyl-epoxy-3,4-epoxycyclohexane	<15	1.18–1.10	1	70–74	227 (760)	0.1	−55

function as initiators, their neutralization will cause a marked decrease in polymerization rate. It may even result in nil reactivity. Coatings such as these are used as conformal coatings [*23–25*] in the electronics industry because of their excellent electrical (MIL-I-46058C approved, QPL Type ER) flammability (UL QMJU2 at a 2-mil thickness) and water permeability properties, as exterior can and other packaging coatings, overprint varnishes, printing inks for paper and metal, etc.

Cycloaliphatic epoxides have been reacted with the free carboxylic acid groups on anhydride adducts of polyols [*26*]. Such coatings are characterized by pot lives of less than 8 h, high solids, and low-temperature curing capabilities with very high gloss and depth of image, high hardness, excellent solvent resistance, adhesion, and toughness. In other instances, the epoxides have been reacted with polyols in the presence of triflic acid salts (as diethylammonium triflate, 3M Co.). In this case, shelf lives of more than eight months have been obtained and the formulated systems have high solids coupled with low viscosity and low temperature-cure characteristics. Cured coatings have an excellent balance of properties similar to those described above.

TABLE 2—A partial listing of polymeric films available for coating or other uses [*27*].

Type Polymer	Available as	
	Conventional Film	Shrink Film
Cellophane	Yes	No
Cellulose acetate	Yes	No
Cellulose acetate-butyrate	Yes	No
Cellulose triacetate	Yes	No
Ethylene/vinyl acetate copolymer	Yes	
Fluorocarbon	Yes	No
Ionomer	Yes	No
Nylon	Yes	Yes
Polycarbonate	Yes	No
Polyester	Yes	Yes
Polyethylene	Yes	Yes
Polyethylene linear low density	Yes	No
Polypropylene, nonoriented	Yes	No
Polypropylene, oriented	Yes	Yes
Polyurethane	Yes	No
Poly(vinyl alcohol)	Yes	No
Poly(vinyl chloride)	Yes	Yes
Polyvinylidine chloride	Yes	Yes

COATING FILMS

Films of many different polymers are available in different forms for use as functional and decorative coatings, adhesive backings, and other uses. Some of these materials [*27,28*] are listed in Table 2. A directory of film manufacturers that lists the manufacturer product name or number and a short description of the product is available [*29*]. Full description of these films and their uses is beyond the intent and scope of this manual.

METALLIC COATINGS [*28,30,31*]

Metallic films are used in a variety of ways. Some metallic coatings are described elsewhere in this manual. The previously described coatings are formulations wherein powdered or flaked metals are combined with a binder. However, solid metallic films are used as coatings in other ways familiar to us. Such films are both functional and decorative in nature. Metals can be applied to plastics and glass by a variety of processes including the physical vapor deposition processes known as vacuum metallizing by thermal evaporation, cathode sputtering, and ion plating of aluminum, copper, chromium, gold, silver, and silicon monoxide [*32*]. Many special effects can be produced including multilayers for cost and protection, iridescent effects by using compounds with high (CeO_2, ZnS) and low (MgF_2, SiO) refractive index, dyeing—particularly of aluminum to achieve a gold color and other colors, and glass coatings on plastic optical parts. Coatings formed by such vacuum deposition processes are most often applied to plastic substrates with end uses for the coated parts including automotive parts, plastic and paper webs for decorative and functional packaging of cosmetics, drugs, clothing, foods, etc., household fixtures, data storage systems, optical components, semiconductor devices, and glass for automotive and architectural applications. As indicated above, the packaging industry has a very large use for thin metallic films on paper and plastic substrates.

A new plasma technique [*33*] known as unbalanced magnetron sputtering (UBM) has advantages over conventional balanced magnetron sputtering (CBM), which is usually used to metalize silicon wafers and architectural glass. In such techniques, an argon plasma is used to remove atoms from a negatively charged target, and magnets are then placed at the outer edges of the target, which is made the cathode. Each of the magnets produces a field of the same strength, and because of this the system is termed "balanced." This conven-

tional system works well when the substrate is silicon and the coating is thin. However, in certain end uses, thick, dense coatings with excellent adhesion are required, and it is herein that UBM has significant advantages for applying coatings of hard, wear-resistant alloys such as TiN, NbN, TiC, CrN, TiNbN, and the like to metal-cutting saw blades and other tools, cams, and gears.

Metallic and ceramic coatings are also applied to metals by a thermal spray technique in which a metallic or ceramic wire, rod, or powder is melted and driven through air or a vacuum at high velocities [*34,35*]. The molten material, which can range from soft, abradable nickel-graphite to hard ceramic zirconia, is deposited on a surface of base metal to which it bonds through chemical and mechanical processes. Thermally sprayed coatings are used as abrasion, corrosion, and heat barriers for expensive machined components, castings, and other parts used in hostile chemical, mechanical, and thermal environments encountered in automotive, spacecraft including aerospace and aircraft, and industrial applications. The special protection provided by these coatings is needed to improve reliability and durability.

Other metal deposition processes for protective, cost savings and/or decorative coating metal, glass, and plastics include electrodeposition by electroplating (Cu, Ni, Cr) and electroless plating (Cu) and galvanizing (Zn). Other than this brief introduction, the metallic coatings mentioned in this short chapter are beyond the scope and intent of the manual and will not be treated further.

SPECIALTY ORGANIC COATINGS

Polysulfides

Liquid polysulfide coatings [*36*] have excellent barrier properties due to low permeability, good chemical and weather resistance, adhesion, low shrinkage, and low-temperature flexibility coupled with good stress relaxation characteristics. These coatings are based on polysulfide polymers prepared

$$HS—(C_2H_4O—CH_2OC_2H_3—S—S)_xC_2H_4OCH_2OC_2H_4SH$$

from bis(2-chloroethyl)formal, 1,2,3-trichloropropane and sodium polysulfide. The polymers are available in a molecular weight range of 1000 to 8000. The thiol or mercaptan end groups of this polymer provide sites for curing in an oxidative manner with manganese dioxide, dicumene hydroperoxide and organic peroxides in general, *p*-quinonedioxime, by reaction with glycidyl epoxides in the presence of tertiary amines, or by reaction with multifunctional isocyanates. The polymers are used as rubbery coatings and sealants in buildings and civil engineering projects requiring excellent ultraviolet light resistance and other general weatherability properties. Polysulfide coatings have been commercially used for over 50 years. The most recent use of the polymers is to provide chemically resistant barrier coatings on chemical-containment storage-tank dikes that protect the environment from chemicals that could cause serious pollution problems.

Phenoxy

Polyhydroxyethers which are commonly known as phenoxy polymers or merely phenoxy, are high-molecular-weight, high-performance thermoplastic materials that are similar in character to the diglycidyl ethers of bisphenol A that are described in Fig. 1 of the manual chapter entitled "Epoxy Resins in Coatings." However, there are significant differences that make the phenoxy polymers separate and unique polymers [*37–39*]. These polymers have the structure

$$—[O—C_6H_4—C(CH_3)_2—C_6H_4—O—CH(OH)—CH_2]_n—$$

where n is about 100, indicating a molecular weight of about 30 000 compared with a molecular weight of about 300 to 10 000 for the diglycidyl ethers of bisphenol A. In addition, phenoxy polymers do not have active epoxide end groups and are thermally stable materials with no limit on shelf life, are tough and ductile, and can form useful, resistant films by solvent evaporation without cross-linking. The hydroxyl functionality associated with phenoxy polymers provides a site for cross-linking with isocyanates, epoxides, or aminoplasts. Films from these polymers are considered to have excellent physical and chemical resistance properties when the polymer is in a thermoplastic form, but if improved resistance to certain solvents is needed, the polymers may be cross-linked. The high molecular weight of these polymers results in relatively low solids (~20%) coating systems, and this might be a restriction to their use in today's climate for high solids. The excellent properties of these polymers has led researchers into investigations of ways for advancing molecular weight of the diglycidyl ethers of bisphenol A during the curing stages [*40*].

Parylene Coatings [*41,42*]

Parylene coatings are applied by exposing a substrate to a gaseous atmosphere of *p*-xylylene. The gaseous monomer is stable, but when it is condensed on a substrate it spontaneously polymerizes to form high-molecular-weight, linear, poly(*p*-xylylene), which is commonly known as parylene [*43*]. The resultant coating of crystalline polymer provides a pinhole-free coating with an outstandingly uniform thickness and conformality even over pointed objects such as a needle. The polymer has excellent electrical properties, including high dielectric breakdown voltage, low dielectric constant and dissipation factor, and high-volume resistivity due to low moisture absorption and freedom from ionic impurities. Parylene is used for coating printed wiring assemblies, semiconductors, capacitors, electrets, contamination and corrosion control, medical and surgical devices, as well as similar end uses that require an inert coating that can be uniformly applied in a very thin film.

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Part 4: Plasticizers

17

Plasticizers

by Peter Tan[1] *and Leonard G. Krauskopf*[2]

PAINT AND COATING FORMULATIONS often incorporate high boiling fluids as plasticizers where rigid or brittle resins fail to meet toughness and flexibility requirements. The primary function of the plasticizer is to impart flexibility to the resin, thus minimizing film cracking. Depending on resin and other ingredients used in the system, plasticizer choice may affect compatibility, toughness, flammability, smoke generation, heat and light stability, and other aging or permanence-related performances. Plasticizers are primarily employed in heavy gage coatings and/or when improved toughness is required for industrial, automotive, and appliance applications.

Plasticizers function by reducing the glass transition temperature of the resin to a point below its application temperature. The chemical mechanism of plasticization involves a strong polar association of polymer-plasticizer molecules, but not a chemical reaction between them. Plasticizers fundamentally reduce Van Der Waals forces between polymer-polymer molecules in the amorphous regions and do not penetrate crystallites [*1–3*]. The plasticized morphological phase is then of a different nature than that of the neat polymer and has unique mechanical properties.

The absence of a chemical bond between the plasticizer and the polymer impairs permanence; plasticizer molecules are free to leave the polymeric coating by means of extraction and volatility. Plasticizer loss, however, is minimal in most applications except for very low molecular weight plasticizers and/or exposure to very severe thermal conditions. Thus, plasticized coatings products have high durability and long service life in most applications. Plasticizers are liquids of molecular weight greater than that of solvents—to limit volatility—but are not solids, such as alloying polymers, etc. It should be noted that cross-linked resinous coatings significantly reduce plasticizer loss due to diffusibility and volatility. Several thousand high boiling fluids are potential plasticizers for coatings applications. The choice of plasticizer is dependent on compatibility with the resin in use, cost, and other desired attributes.

Plasticizers may be classified by both chemical structure and performance characteristics, as shown in Table 1 [*4*]. Typical plasticizers are liquid esters of molecular weight between about 200 to 800, with specific gravities between 0.75 and 1.35 at 20/20°C, viscosities between 50 to 450 cSt, vapor pressure of less than 3.0 mm of mercury at 200°C, and flash points greater than 120°C (248°F). They are generally stable and innocuous and should not be considered a significant threat to humans or the environment [*5–6*].

Plasticizer extenders are commonly used in extruded or molded flexible plastic shapes. Extenders are low-cost organic oils that may be subdivided as groups of aliphatic, aromatic, or chlorinated hydrocarbons. They are seldom used in coatings due to their relatively high volatility and limited compatibility in polar resins.

This chapter lists the basic properties of plasticizers and methods for their determination. Methods for the isolation, identification, and quantitative determinations of these plasticizers are also included.

PHYSICAL AND CHEMICAL PROPERTIES

Acidity

Plasticizer acidity may be due to improper processing, degradation during storage, contamination, presence of by-products, or residual catalyst. ASTM Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products (D 1613) may be used for determination of acidity. Either ethyl or isopropyl alcohol may be used as diluent for the plasticizer, which is titrated with aqueous sodium hydroxide or potassium hydroxide to the phenolphthalein end point. Results may be expressed in weight percent, as weight equivalents of acetic acid, acid number (milligrams potassium hydroxide consumed per gram of sample), or if the plasticizer is an ester, as weight percent of the parent acid of the ester (see section entitled "Ester Value").

Color

The majority of plasticizers are colorless. As a class, esters are very stable chemical reagents. However, exposure to abnormal conditions such as high thermal or ultra-violet energy, moisture, or chemically active surfaces may induce development of color bodies and/or chemical decomposition of the plasticizers. Higher molecular weight phthalates, polymeric plasticizers, and chlorinated paraffins may range in color from light to bright yellow. ASTM Test Method for Color of Clear Liquids (Platinum-Cobalt Scale) (D 1209) is the standard color measurement method for plasticizers.

[1]Manager, Marketing Technical Services, Exxon Chemical Asia PTE LTD, Intermediates Technology Center, Block 14 (Maxwell) No. 02-03, Science Park Drive, Singapore 0511.

[2]Research associate, Exxon Chemical Company, Intermediates Technology, P.O. Box 241, Baton Rouge, LA 70821.

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TABLE 1—Plasticizer family/performance grid.

Family	General Purpose	Strong Solvating	Low Volatility	Low Temperature	Low Diffusibility	Flame Resistant	Stabilizer
Phthalates	X	√	√	√	√	...	...
Trimellitates	...	...	X	√	√	...	...
Aliphatic dibasic esters	...	...	...	X	...	...	...
Phosphates	...	√	...	√	...	X	...
Epoxides	...	...	√	√	...	...	X
Polyesters	...	...	√	...	X	...	...
Extenders	X	...	...	√	...	...	...

NOTE: X = Primary performance function.
Source: Society of Plastics Engineers, Regional Technical Conference (SPE, RETEC) Vinyl I; 1992; reprinted with permission.

APHA is a scale that is likewise used for liquids of low color. The standards are based on platinum solutions without cobalt and are described in ASTM Standard Method of Testing Urethane Foam Polyol Raw Materials (D 2849).

ASTM Test Method for Color of Transparent Liquids (D 1544) employs the Gardner Color Scale for amber and dark-colored plasticizers which cannot be read on the platinum-cobalt (Pt-Co) or APHA scales. Gardner standards are colored disks held in a "Hellige" gage. Gardner values of "1" and "2" are approximately equivalent to 250 and 400, respectively, on the APHA scale. The Gardner scale goes up to "18" for use with increasingly darker amber and brownish color liquids.

The platinum-cobalt scale is also known as the Hazen scale, but readers should be aware of potential confusion with The American Public Health Association (APHA); APHA adopted a version of this scale in which a Hazen color of one is the same as APHA 100. To avoid confusion, it is recommended that only the Pt-Co scale be used when referring to Procedure D 1209.

The APHA color scale in ASTM D 2849 reflects a slightly greenish hue for APHA versus the Pt-Co scale, which is slightly yellowish. The scale readings are similar in the 25 to 50 range, but in the vicinity of 100 Pt-Co, the APHA scale (Pt only) reads 10 to 20 units lighter (lower). Both the Pt-Co and APHA scales cover a range from "3" up to "500," but are recommended for use for liquids having colors ≤250 units.

An instrumental method (Hunter Colorimeter) that is five to seven times more precise may also be used for color measurement, replacing the subjective comparisons of the above methods using Nessler tubes; while commonly used in commercial practice, the Hunter Colorimeter is not yet defined as an ASTM method.

Copper Corrosion

ASTM Test Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test (D 130), and ASTM Test Method for Copper Corrosion of Industrial Aromatic Hydrocarbons (D 849), which is normally applied to hydrocarbon solvents, may be used to evaluate the copper corrosive tendencies if suspected to be sourced in plasticizer. The appearance of a copper strip, which has been immersed in the test fluid, under standard conditions, is compared with twelve special standard strips classified as follow:

1. Slight tarnish (1a,b) light orange, dark orange.
2. Moderate tarnish (2a,b,c,d,e) claret red, brassy, or gold.
3. Dark tarnish (3a,b) magenta, multicolored.
4. Corrosion (4a,b,c) transparent black, jet black.

The historical application of copper corrosion testing to plasticizers was an attempt to measure effects contributed by residual sulfur compounds due to sulfur-based catalysts, which may hydrolyze to acidic pH in the presence of moisture. Current commercial grade plasticizers do not typically contribute to copper corrosion. Commercial grade alkyl sulfonate esters of phenol [7] are plasticizers in which the sulfur is organically "combined" and not readily susceptible to hydrolyses.

Distillation Range

Most plasticizers have high boiling points or boiling ranges. This property can be used as a measure of its degree of permanence or resistance to loss through volatilization. Presence of lighter components can also be detected. The measurement of vapor pressure is a costly and time-consuming procedure. Thus, commercial liquids of high molecular weight—low vapor pressures—are typically characterized by boiling ranges in which one determines initial, mid, and final (or drypoint) boiling point temperatures. For fluids with dry point >140°C, ASTM Test Method for Distillation of Petroleum Products (D 86) is used. Fluids with dry point <140°C are measured using ASTM Test Method for Distillation Range of Volatile Organic Liquids (D 1078). For very high boiling fluids or where decomposition may occur, distillation may be done under vacuum regulated at 5 mm Hg. The initial and final boiling points or the mid boiling point are typically reported.

Gas chromatographic (GC) techniques are commonly applied as a fundamental measure of plasticizer chemical purity and isomer distribution. Direct relationships between GC traces and boiling ranges have not yet been established for plasticizers.

Both distillation range and GC analyses are means to relate vaporization characteristics of plasticizers to practical needs. The fundamental characteristic of vapor pressure may be measured by ASTM Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope (D 2879). The log of plasticizer vapor pressure varies linearly with the reciprocal absolute temperature (degrees Kelvin) according to the Clausius-Clapeyron equation [8]

$$\ln\frac{P_1}{P_2} = \frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{1}$$

where

P_1 and P_2 = vapor pressure, $g \cdot cm^2 \cdot s^{-2}$,
T_1 and T_2 = respective temperatures, K,
ΔH = molar heat of vaporization, $cal \cdot g^{-1}$, and
R = gas constant, 1.99 cal $°C^{-1} \cdot mol$.

Vapor pressure values are useful to estimate normal boiling points at 760 mm mercury and solubility parameters [*1*]. Sears and Darby have reported that the vapor pressure of binary plasticizer blends may be expected to fall between the values of the neat plasticizers, but cannot be predicted from a knowledge of the blend ratio and the neat vapor pressures.

Ester Value

Esters are the largest group of materials that are commercially useful as plasticizers. This is a result of reasonable costs and broad utility in a wide range of polymers having moderate to high polarity characteristics. Ester value can be used to estimate the purity or ester content of the plasticizer. ASTM Test Method for Ester Value of Lacquer Solvents and Thinners (D 1617) or ASTM Methods of Sampling and Testing Plasticizers Used in Plastics (D 1045) may be used for this determination. The methods involve saponification of the ester in a known excess amount of KOH. The excess amount of KOH is then determined by titration with standard sulfuric acid. The amount of KOH consumed in the saponification process is a measure of the ester content of the plasticizer.

A gas chromatography method, ASTM Test Method for Purity of Monomeric Plasticizers by Gas Chromatography (D 3465), may also be used to determine the purity of monomeric plasticizers. The GC method does not provide "ester values." It is useful to characterize major isomers present versus known standards and to ascertain trace quantities of nonparent organic compounds. GC instrumentation is costly and requires comparison of output traces against a library of known materials that have been characterized under a specific set of conditions using specific GC instruments and columns.

Flash Point

Most plasticizers are high flash materials. Either ASTM Test Method for Flash and Fire Points by Cleveland Open Cup (D 92) or ASTM Test Method for Flash Point by Pensky-Martens Closed Tester (D 93) may be used. Preference should be for the closed cup method; this yields a more conservative number and is consistent with Department of Transportation (DOT) regulations in the United States. DOT has revised the definitions and classifications of hazardous materials, effective 1 Oct. 1993, as follows:

	Flash Point
Not Regulated	≥93°C (200°F)
Combustible	61 to 92.5°C (142 to 199°F)
Flammable	≤60.5°C (141°F)

The "flash point" is defined as the minimum temperature at which a liquid gives off vapor within a test vessel in sufficient concentration to form an ignitable mixture with air near the surface of the liquid as determined by ASTM Test Method for Flash Point by Tag Closed Tester (D 56) or ASTM Test Methods for Flash Point of Liquids by Setaflash Closed Cup Apparatus (D 3278).

Flash point values are reported for commercially significant monomeric plasticizers in E. J. Wickson's *Handbook on PVC Formulating* [*7*]. While not a very good analytical tool, flash points will reflect presence of nonparent, low-flash-point contaminants.

Pour Point

Due to the high molecular weight and isomeric mixtures of plasticizers, few have distinct freezing points. The pour point can be useful information for handling plasticizers during cold seasons. Method of measurement is described in ASTM Test Methods for Pour Point of Petroleum Oils (D 97). Plasticizer pour point temperatures may also be estimated from viscosity/temperature plots as the temperature at which kinematic viscosity is 50 000 cSt. Most plasticizers have pour points of less than −30°C [*7*]; no known relationship exists between pour point and plasticizer performance properties in polymers under low-temperature conditions.

Refractive Index

The refractive index of a plasticizer is measured using ASTM Test Method for Refractive Index and Refractive Dispersion of Hydrocarbon Liquids (D 1218). Refractive index is often thought of as a means of identifying the plasticizer. This is an erroneous assumption. It may be used, however, to differentiate between classes of plasticizers, as, for example, between phthalates and adipates [*10*]. When used with other physical measurements, refractive index may be used as a supplemental test. Refractive index can also be used to check for product contamination, but it is only useful to distinctify commercial materials having very widely different refractive indices.

Residual Odor

Residual odor may be contributed by reaction by-products from manufacturing or by residual raw ingredients which are often more volatile and odorous than the plasticizer. When ASTM Test Method for Odor of Volatile Solvents and Diluents (D 1296) is used, tests at elevated temperatures (about 150°C) can be considered to improve detection. Since odor is a subjective characteristic, generalizations for plasticizers are limited to terms such as "mild and characteristic."

Sampling

To obtain representative samples of plasticizers for evaluation, ASTM Methods for Sampling and Testing Plasticizers Used in Plastics (D 1045) may be followed. ASTM Recommended Practice for Sampling of Industrial Chemicals (E 300) can also be used.

Density and Specific Gravity

Density is an important characteristic for design engineering of plasticizer storage and building facilities. Specific gravity is the density of the given reagent relative to that of water

at the specified temperature; it is generally used in the characterization of plasticizers or as a means to detect gross contamination. Specific gravity at 20/20°C is measured with ASTM Test Methods for Specific Gravity of Liquid Industrial Chemicals (D 891) and is commonly employed in industry. Commercial plasticizers typically fall within the range of 0.92 to 1.50 sp gr at 20/20°C. ASTM Test Method for Density and Relative Density of Liquids by Digital Density Meter (D 4052) is the recommended procedure to measure specific gravity of fluids that lie between 0.68 and 0.97; this method is applicable to hydrocarbons that are commonly used as plasticizer extenders.

Viscosity

Viscosity measures the fluid's resistance to flow; the thicker the fluid, the higher its viscosity and the greater its resistance to flow under gravity. In ASTM Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity) (D 445), time is measured in seconds for a fixed volume of the fluid to flow under gravity through the capillary of a calibrated viscometer at constant temperature. The kinematic viscosity of a plasticizer varies as a log log function versus the log of absolute temperature according to the following equation

$$\log \log \eta \cong A - B \log T \qquad (2)$$

where

η = kinematic viscosity, centistokes,
T = temperature, degrees Kelvin, and
A and B = constants.

This reflects the tremendous influence of temperature on viscosity and allows one to interpolate viscosity values at specified temperatures. The kinematic viscosity (centistokes) can be converted to its dynamic viscosity (centipoise) by multiplying by the true density of the fluid at the specified temperature: dynamic viscosity, cP = kinematic viscosity, cSt, times density.

Water

Residual water from manufacturing processes and moisture absorbed from the atmosphere can affect the quality and clarity of coatings. Water content can be measured using ASTM Test Method for Water in Volatile Solvents (Fischer Reagent Titration Method) (D 1364). Plasticizers are hydrophobic liquids and typically have a limited capacity to take up water and/or be dissolved into water. Higher-molecular-weight phthalates are practically insoluble in water with solubilities in the 0.1 to 1.2 mg/L (ppm) range with even less solubility in salt water [*6*].

Typical Properties

As shown in Table 1, commercial plasticizers fall into about seven chemical family groups (eight if we were to add a "miscellaneous" grouping). The major plasticizer types in use are phthalates, trimellitates, and aliphatic dibasic esters such as adipates. The families of esters are formed by reacting the parent acid with monomeric alcohols ranging from C_4H_9OH (butanol) to $C_{13}H_{27}OH$ (tridecanol); the alcohol may also vary in isomeric structure ranging from normal (unbranched) to very specific and/or randomly branched structures. Two alcohols have found wide usage in synthesis of commercial plasticizers—2-ethylhexanol and isononanol—a mixture of randomly branched (primarily methyl branched) nonyl isomers. Table 2 is a summary of typical properties of plasticizers derived from these two alcohols with the major parent acids—phthalic, trimellitic, and adipic [*11*].

METHODS OF IDENTIFICATION

A plasticizer may initially be characterized by its functional groups. While absolute identification is complicated without sophisticated chemical or instrumental methods, it is possible to identify the type of plasticizer by functional groups or presence of elements associated only with the plasticizer by the use of infrared analyses or wet chemistry. Most plasticizers are a member of one of the following families:

Plasticizer Type/Functional Group
Adipates
Chlorinated compounds
Epoxides (oxirane)
Phosphates
Phthalates
Polyesters
Trimellitates

Isolation of Plasticizers

Plasticizers may be separated from a lacquer or dried film by solvent extraction if it is to be analyzed. The lacquer is first dried to remove all solvents present. The dried solid is then solvent extracted (in an appropriate apparatus) with hot ethyl ether or another appropriate solvent that will extract the plasticizers while leaving most of the resins behind. The extractant is concentrated, and a small amount of methyl or ethyl alcohol is added. This will cause some of the dissolved resin to precipitate out. Next, filter and concentrate the extractant. ASTM Test Method for Acetone Extraction of Phenolic Molded or Laminated Products (D 494) may be applied.

Instrumental Methods

Modern instrumental analytical methods are able to separate, identify, and quantify components in composite mixtures. Rapidly falling costs of such instruments have enabled instrumental methods to be more widely available. These include gas chromatography (GC), high-performance liquid chromatography (HPLC), infrared spectroscopy (FTIR), and other emerging analytical instruments like supercritical fluid chromatography (SFC), GC/FTIR, and GC/MS (mass spectrometry).

Infrared Spectrophotometry

An infrared scan of the isolated plasticizer is by far the best way to identify the functional groups in the molecule. Mixtures of plasticizers can present problems due to masking effects. If one or more of the component plasticizers is known and its IR scan available, subtracting it from the IR scan of

TABLE 2—Typical physical properties of plasticizer esters made with isononyl and 2-ethylhexyl alcohols.

	Phthalate		Trimellitate		Adipate	
	DOP	DINP	TOTM	TINTM	DOA	DINA
Alkyl	2EH	INA	2EH	INA	2EH	INA
Molecular weight	390	424	546	596	370	404
Specific gravity at 20/20°C (68°F)	0.986	0.973	0.992	0.979	0.927	0.924
Refractive Index n_D^{20}	1.484	1.486	1.482	1.484	1.445	1.449
Viscosity, cSt at 20°C	83	102	312	430	16	26
Pour point, °C	−47	−48	−46	−40	<−60	−59
Vapor pressure, mm Hg at 200°C	1.2	0.5	0.08	0.03	2.5	1.5
Mid boiling point, °C at 5 mm Hg	230	245	300	331	215	233
Flash point, °C	204	213	221	241	193	199
Color, Pt-Co	<25	<25	<100	<100	<25	<25

Source: Edenbaum, J., *Plastics Additives and Modifiers Handbook*, Van Nostrand Reinhold, New York, 1992, p. 362. Reprinted with permission.

NOTE: DOP di(2-ethylhexyl) phthalate
DINP di (isononyl) phthalate
TOTM tris(2-ethylhexyl) trimellitate
TINTM tris(isononyl) trimellitate
DOA di(2-ethylhexyl) adipate
DINA di(isononyl) adipate

the mixture may aid in identification of the other component. Other chromatographic techniques could be used to separate the components before scanning.

Liquid Chromatography

Column chromatography involves distribution of substances between liquid (mobile phase) and substrate (solid phase). Column and thin layer chromatography can be used. Instrumental methods using high-performance liquid chromatography (HPLC) with ultraviolet detection can be used for separation, identification, and quantification of plasticizers which possess a suitable chromophore.

Gas Chromatography

By comparing relative retention times and peak shapes with known samples, a plasticizer or mixture can often be identified and quantified. When coupled with IR (i.e., GC/FTIR), the IR spectrum of each chromatographic peak can assist in the identification of functional groups and hence plasticizer identity.

Qualitative Methods

For the detection of nitrogen, chlorine, sulphur, or phosphorus, the sample needs to be fused with metallic sodium. This preparation should be carried out in a fume hood and caution observed when handling metallic sodium. A small amount (about 3 mm^3) of metallic sodium is placed in a dry 6-in. (15.24-cm) test tube. The test tube should be held vertically by clamping it at the open end. The test tube is then heated until a cloud of sodium vapor begins to form. Remove the flame immediately. Add two to three drops of the plasticizer sample directly to the sodium vapor. When the test tube is cold, break off the end with the sodium in a mortar. Add several milliliters of alcohol to destroy unreacted sodium. Add about 20 mL of distilled or deionized water, grind up the sample, transfer to a beaker, bring to boil, and filter. The filtrate is then used for the chemical detection of the elements.

Sulfur

Add two to three drops of 10% solution of lead acetate to 2 mL of a 10% solution of sodium hydroxide. Add this mixture to 5 mL of the filtrate. A black precipitate of lead sulphide indicates the presence of sulphur. Positive identification suggests that the sample is either a sulphonamide or sulphate.

Nitrogen

Bring 2 mL of the filtrate to boil in a test tube. Add five drops of a 10% solution of NaOH and five drops of 10% ferrous sulphate solution. When cold, add, dropwise, a 10% solution of hydrochloric acid until the solution is acidic and the precipitate of ferrous hydroxide has dissolved. Avoid using an excessive amount of acid. A blue or green color or blue precipitate indicates presence of nitrogen. A positive test suggests that the plasticizer could be an amide.

Chlorine

Acidify 5 mL of the filtrate with several drops of dilute sulfuric acid and bring it to boil. Cool and acidify with nitric acid. Add several drops of a 10% silver nitrate solution. A white precipitate indicates the presence of a chlorinated compound.

Phosphorus

Boil 5 mL of the filtrate with 3 mL of concentrated nitric acid for 1 min. Cool and add twice the volume of 10% ammonium molybdate solution. Heat to about 60°C and set aside to cool. A yellow precipitate indicates the presence of phosphorus. Phosphate plasticizers will result in a positive test.

Phthalates

Add about 0.05 g of resorcinol and 0.05 g of phenol to separate 6-in. (15.24-cm) test tubes. Add to each test tube two to three drops of the isolated plasticizer and a drop of concen-

trated sulfuric acid. Heat the contents in an oil bath at 160°C for several minutes. Cool and add 2 mL of distilled water and 2 mL of 10% sodium hydroxide solution and stir. The presence of phthalate is indicated by a pronounced green fluorescence in the tube with resorcinol, and the tube with phenol will be red.

PERFORMANCE PROPERTIES

Compatibility

Compatibility is the ability of two or more substances to mix together without objectionable separation [*12*]. In the case of plasticizers, it is primarily a measure of the solvency or strength of positive interactions between the plasticizer and the polymer which attract them together.

Solvency is the extent (or amount) of interaction of plasticizer or solvent molecules at the surface of a polymer particle; a solid solution results when the polymer and plasticizer—and possibly additional reagents—become molecularly homogeneous. The degree to which a homogeneous solution, or miscibility, is stable is a function of the plasticizer/polymer interactions when in the presence of other reagents employed in the coating formulation; it must be recognized that the presence of these additional reagents can compete with the polymer/plasticizer interactions. The rule of thumb "like dissolves like" applies, but more specific knowledge is required to avoid results that appear to be anomalous.

Dried polymeric coatings may be considered as solid solutions; the limits of miscibility are impacted by all of the reagents that become components of the coating—those intentionally added, as well as inadvertent contaminates and/or degradation products formed in the coating process. When plasticizers are employed, they have a major effect on compatibility, primarily due to the level, or concentration, used in the polymer. If we accept the definition of a solution as a homogeneous mixture of two or more types of molecules, then "solvency" is a measure of a given solvent or plasticizer to homogenize and interact with a given polymer. Quantification of this "interaction" has been elusive; scales which have been devised are capable of measuring only gross differences. Observations of phase separation of plasticizer/polymer have been more finite than that predicted in many cases, while on the other hand, observations of symptoms (compatibility) are incapable of separating "solvency" from other interfering mechanisms that are concurrent, such as diffusibility.

Hansen publications [*13–14*] define the total solubility parameters of polymers, solvents, and other reagents as a function of three component parameters:

$$\lambda_T = (\lambda_d^2 + \lambda_p^2 + \lambda_h^2)^{1/2}, (\text{cal/cm}^3)^{1/2} \quad (3)$$

where

λ_T = total solubility parameter,
λ_d = dispersion parameter,
λ_p = polarity parameter, and
λ_h = hydrogen bonding parameter.

The location of polymers and other non-ionic reagents may be defined on this three-dimensional grid. Hansen states that it may be assumed that the closer a plasticizer lies to the center of the polymer solubility space of a polymer, the more compatible it will be with the given polymer. Many materials have been characterized in this fashion. Exxon Chemical Company has developed a computerized capability to define the location of various solvents and plasticizers relative to that of various polymers; it is called the CO-ACT® program and contains information on more than 1200 resins, solvents, and plasticizers [*15*].

Compatibility data for different plasticizer resin systems are available in various publications [*1,16–17*]. The plasticizers are usually presented as compatible, incompatible, or partially compatible with the resins. These data are often not useful due to incomplete description of the resin or a lack of standard approach in the test and reporting of observations. Where Hansen parameters are available for the plasticizers and resins, comparison of three-dimensional Hansen solubility parameters provide a better measure of compatibility as described earlier. Table 3 lists generalized examples of plasticizers and their compatibility with various coating resins.

Permanence

"Reactive" plasticizers are specialty types designed to self-polymerize or graft onto the polymeric resin during the curing process. But, in most cases, plasticizers do not chemically react with the polymer. They function by an overall solvating action that is less strong than that of a good solvent, but stronger than that of incompatible reagents such as lubricants. This interaction imparts a slight effect on plasticizer "permanence," or more properly "transience." One of two factors are generally the controlling influence over loss of plasticizer:

- Rate of diffusion of plasticizer from the resin bulk to the surface.
- Rate of loss of plasticizer from the surface.

The slowest rate of the two is the controlling factor under any specific set of conditions. Volatility and extraction by aqueous reagents are generally surface-controlled losses, while rate of diffusion controls loss under oil immersion and similar tests. The subject is very complex [*1–2*], but one may consider plasticizer vapor pressure as a key predictor of volatile loss, while diffusion-controlled losses are improved with plasticizers of higher molecular weight and branchiness in the chemical structure.

Resistance to washing is typically characterized as a function of thermal and/or humidity cycling exposures. This is a measure of the aging resistance of the plasticized polymeric coating.

Low-Temperature Properties

Some applications require flexibility and impact resistance at low temperatures. This property may be significantly improved at increased plasticizer levels, as well as being a function of the plasticizer type [*1*]. For example, at approximately 50 PHR, plasticizer in poly(vinyl chloride) phthalates of linear alcohols impart about −10°C improvement in low-temperature brittleness over branched, DOP-type, phthalate plasticizer. Dialkyl adipates, however, impart about −25°C improvement over the brittleness value of DOP-plasticized PVC as measured by ASTM Test Method for Brittleness Temperature of Plastics and Elastomers by Impact (D 746).

TABLE 3—Plasticizers and their compatibility with coating resins.

Plasticizer	CA	CAB	CN	EC	PMMA	PS	VAc	VB	PVC	VC/VAc
Phthalates										
DOP	I	C	C	C	C	C	I	P	C	C
DIOP	I	C	C	C	C	C	C	P	C	C
DINP	P	C	C	C	C	C	C	P	C	C
DIDP	P	C	C	C	P	C	P	P	C	C
Trimellitates										
TOTM	P	C	C	C	P	C	P	P	C	C
TINTM	P	C	C	C	P	C	P	P	C	C
Phosphates										
TCP	C	C	C	C	P	C	C	C	C	C
TOP	P	P	C	C	I	C	I	C	C	C
Acyclic esters										
DOA	P	C	C	C	P	C	P	P	C	C
DINA	P	C	C	C	P	C	P	P	C	C
DOZ	P	C	C	C	P	C	P	P	C	C
DOS	P	C	C	C	P	C	P	P	C	C
Epoxidized										
Soybean oil	I	P	C	C	I	I	I	I	C	C
(2EH) tallate	I	C	C	C	I	I	I	C	C	C
Polyesters										
Adipic/Diol	P	C	C	C	P	C	P	P	C	C
Phthalic/Diol	P	C	C	C	P	C	P	P	C	C

C = Compatible; P = Partially compatible; I = Incompatible.

RESINS

CA = Cellulose Acetate
CAB = Cellulose Acetate/Butyrate
CN = Cellulose Nitrate
EC = Ethyl Cellulose
PMMA = Methyl Methacrylate
PS = Polystyrene
VAc = Vinyl Acetate
VB = Vinyl Butyral; 19 wt% Vinyl Alcohol
PVC = Vinyl Chloride
VC/VAc = Vinyl Chloride/Vinyl Acetate Copolymer: 90/10

PLASTICIZERS

Phthalates
DOP = di(2-ethylhexyl)
DIOP = di(isooctyl)
DINP = di(isononyl)
DIDP = di(isodecyl)

Trimellitates
TOTM = tris(2-ethylhexyl)
TINTM = tris(isononyl)

Acyclic Esters
DOA = di(2-ethylhexyl) adipate
DINA = di(isononyl) adipate
DOZ = di(2-ethylhexyl) azelate
DOS = di(2-ethylhexyl) sebacate

NOTE: Compatibility of plasticizers in specific polymers is a function of relative concentration (PHR), as well as the presence of other formulating reagents and residuals present in polymers. The above ratings are based on plasticizer levels typically used in coatings applications (<40 PHR).

Commercial coatings require the optimum choice of plasticizer type and concentration to meet required costs, hardness or modulus, permanence, and low-temperature properties.

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Part 5: Solvents

18

Solvents

by Stephen A. Yuhas, Jr.[1]

SOLVENTS ARE SUBSTANCES, usually liquids, which are capable of dissolving other substances to bring them into liquid form. In paints and coatings, solvents dissolve the solid or semi-solid film-forming resins and reduce viscosity so that the paint can be applied as a uniform, thin film to a surface. Although solvents are transient components of a paint, they significantly affect not only the application characteristics of a paint, but also the appearance, physical properties, and durability of the coating.

The two most important performance requirements that must be considered in selecting the proper solvent for any end use are solvency and evaporation rate. These key properties control initial paint viscosity during application, coating viscosity at various stages of drying, and final coating appearance. Solvents must evaporate relatively quickly during initial drying to prevent excessive flow and sag, but must evaporate more slowly in the later stage to provide good leveling and adhesion.

Solvency and evaporation rate are often measured indirectly since direct measurements are not always feasible or convenient. In addition, there are numerous other solvent properties that must be considered for specific applications. These are often listed as requirements in the solvent specifications and include measures of purity, uniformity, safety, and compliance with air pollution regulations.

There are many different solvents used by the coatings industry. To facilitate their review and comparision, it is convenient to classify them chemically into three general categories: hydrocarbons, oxygenated, and others. Each category will be discussed separately in the sections that follow.

Solvents may also be classified according to the function they perform: active, latent, and diluent. An active solvent is a true solvent for the film-forming resin and has the major role in dissolving it. A latent solvent alone will not dissolve the resin, but behaves as an active solvent or has a synergistic effect when used in combination with an active solvent. A diluent usually has no solvency for the resin, but is tolerated by it in blends. Diluents are added to reduce cost and vehicle viscosity through dilution.

CLASSIFICATION BY CHEMICAL TYPE

Solvents can be broadly classified by chemical type into three categories:

1. *Hydrocarbon solvents*—organic compounds comprised of molecules consisting only of hydrogen and carbon atoms.
2. *Oxygenated solvents*—organic compounds comprised of molecules consisting of hydrogen, carbon, and oxygen atoms.
3. *Other solvents*—organic compounds consisting of hydrogen, carbon, and atoms other than oxygen, such as chlorine or nitrogen, or inorganic compounds such as water or supercritical carbon dioxide.

Hydrocarbon Solvents

The vast majority of hydrocarbon solvents are derived from petroleum, although a few are of vegetable origin. Therefore, hydrocarbon solvents may be regarded as being "natural products." Most are physically separated from petroleum by distillation and other refining processes. As a result, hydrocarbon solvents tend to be mixtures of organic compounds (rather than pure chemicals), and they may vary in composition depending on feedstock source.

Solvency of hydrocarbons is relatively weak compared with oxygenated and other solvents. Being of natural origin, they are good solvents for natural resins and natural-modified resins such as drying oils, varnishes, alkyds, asphalt, rosin, and petroleum resins. However, they are generally poor solvents for synthetic resins such as vinyls, epoxies, urethanes, acrylics, and nitrocellulose. Hydrocarbon solvents are usually used as low-cost diluents in solvent blends. Other distinguishing characteristics of hydrocarbon solvents are low specific gravity and complete water immiscibility.

Hydrocarbon solvents may be further subclassified into four subcategories: aliphatics, aromatics, naphthenes, and terpenes.

Aliphatic Hydrocarbons

Most aliphatic hydrocarbon solvents are manufactured by distilling the appropriate boiling range fractions from crude oil and subsequently treating them to improve odor and color stability. These saturated organic molecules are generally mixtures of straight chain or *normal*-paraffins and branched chain or *iso*-paraffins, with perhaps some cycloparaffins [*1*].

Unique, distinguishing characteristics of commodity aliphatic hydrocarbons are: very weak solvency, low odor, specific gravity, and cost. Although they are active solvents for some varnishes and alkyds, they are used primarily as low-cost diluents in solvent blends. Weak solvency is not necessarily a disadvantage of aliphatic hydrocarbons. They are preferred as carrier solvents in vinyl organosols and as reaction

[1]Chemical engineer, technical consultant, Solventures, Inc., 56 Wick Drive, Fords, NJ 08863.

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diluents in certain polymer syntheses because of their low tendency to dissolve or swell polymers.

Examples of some typical aliphatic solvents used by the coatings industry are shown in Table 1 together with their ASTM specification references. Others are commercially available as aliphatic naphthas having producer-defined distillation ranges. The fastest-evaporating solvents—hexane, heptane, and lacquer diluent—are often used as the diluent component of fast-drying lacquers, where one of their important functions is to reduce cost.

Mineral spirits is the most commonly used aliphatic solvent. (Outside the United States, mineral spirits is often called white spirits.) It is the common "paint thinner" sold in retail stores and is used in architectural paints, varnishes, and stains. It has the right combination of moderate solvency and moderately slow evaporation rate to impart proper brushability, leveling, and wet edge.

Mineral spirits is a distillation fraction boiling between 300°F (149°C) and 400°F (204°C), with a minimum flash point of 100°F (38°C). Four types are defined in ASTM D 235, Specification for Mineral Spirits (Petroleum Spirits) (Hydrocarbon Drycleaning Solvent). "Low dry point" mineral spirits, referred to as Stoddard solvent, has a faster evaporation rate and is used as a dry-cleaning solvent.

VM&P naphthas have about the same solvency as mineral spirits, but have a much faster evaporation rate. They are distillation fractions having boiling ranges between 250°F (121°C) and 300°F (149°C). ASTM D 3735, Specification for VM&P naphthas, defines three types. They are used primarily in spray-applied, industrial finishes.

Several hydrocarbon solvent producers also manufacture and market complete lines of pure, isoparaffinic solvents, which are synthetically produced from pure petroleum components. Unique characteristics of the isoparaffins are that they have very weak solvency and are virtually odorless. Examples are odorless mineral spirits and odorless VM&P naphtha.

Aromatic Hydrocarbons

Aromatic hydrocarbons, which are cyclic, unsaturated compounds, are also made from petroleum. However, their manufacture requires additional processing steps. An aliphatic naphtha distillate from crude oil is processed through a catalytic reformer to rearrange the molecules into cyclic and polycyclic compounds, which are further dehydrogenated to aromatics. Various aromatic solvents are then separated by distillation [*1*].

There are only four aromatic solvents commonly used by the coatings industry: toluene, mixed xylenes, and two high-flash aromatic naphthas. Evaporation rates of these four major aromatic solvents range from fast to very slow. ASTM specification references and key properties are summarized in Table 2. Distinguishing characteristics of aromatic solvents, relative to hydrocarbon solvents, are stronger solvency and odor, high specific gravity, and higher cost.

Toluene is a pure chemical, methylbenzene. It is a fast-evaporating solvent used as an active solvent for certain resins, as a lacquer diluent, in spray paints, aerosols, and in a variety of industrial coatings.

Mixed xylenes are used as paint solvents and in thinners. Xylene is a mixture of three isomers: *ortho*-, *meta*-, and *para*xylene, plus ethylbenzene. Solvent xylene from different producers may vary in composition, resulting in slight differences in properties and performance [*2*]. Xylene has a moderate evaporation rate and is used primarily in industrial coatings.

The individual components of mixed xylene solvent are also isolated and marketed separately as chemical intermediates which are used by the coatings and chemical industries. Phthalic anhydride, used in the manufacture of alkyd resins, is produced from *ortho*xylene. Terephthalic acid, also used in the manufacture of resins, is produced from *para*xylene. Styrene is produced from ethylbenzene.

Two *high-flash aromatic naphthas* round out the aromatics most commonly used by the coatings industry.

Type I—Aromatic 100 has a flash point not less than 100°F (38°C).

Type II—Aromatic 150 has a flash point not less than 150°F (60°C).

Aromatic 100 consists mainly of C_9 aromatics, while Aromatic 150 is a mixture of predominantly C_{10} aromatics. Both are slow evaporating and are used in baked industrial coatings.

TABLE 1—Typical properties of selected aliphatic hydrocarbon solvents.

Solvent	ASTM Specification	Specific Gravity, 60/60°F	Distillation Range, °C	Evaporation Rate, *n*-BuAc = 100	Flash Point, TCC, °F (°C)	Kauri-Butanol Value	Aniline Point, °F (°C)
Hexanes	D 1836	0.68	64–70	1500	<0 (< −18)	32	150 (66)
Heptane	...	0.73	94–99	600	18 (−8)	36	129 (54)
Lacquer diluent	...	0.75	93–115	400	20 (−7)	40	120 (49)
VM&P naphthas	D 3735						
Type I "Regular"		0.75	120–150	200	41 (5)	38	117 (47)
Type II "High Flash"		0.76	140–175	150	81 (27)	40	110 (43)
Type III "Odorless"[a]		0.72	120–150	210	41 (5)	29	165 (74)
Mineral spirits	D 235						
Type I "Regular"		0.79	150–210	10	108 (42)	37	130 (54)
Type II "High Flash"		0.79	177–210	8	142 (61)	36	135 (57)
Type III "Odorless"[a]		0.76	150–210	10	104 (40)	27	184 (84)
Type IV "Low Dry Point," "Stoddard Solvent"		0.77	150–185	15	104 (40)	38	123 (51)
Deodorized kerosene	...	0.81	177–265	2	142 (61)	30	160 (71)

[a]Isoparaffinic hydrocarbon.

TABLE 2—Typical properties of selected aromatic hydrocarbon solvents.

Solvent	ASTM Specification	Specific Gravity, 60/60°F	Distillation Range, °C	Evaporation Rate, *n*-BuAc = 100	Flash Point, TCC, °F (°C)	Kauri-Butanol Value	Mixed Aniline Point, °F (°C)
Toluene	D 841	0.872	110–111	180	45 (7)	105	48 (9)
Mixed xylenes	D 843	0.871	137–142	70	83 (28)	98	51 (10)
ortho-xylene	D 4076	0.885	143–145	65	90 (32)	106	51 (10)
meta-xylene	...	0.869	139–140	70	81 (27)	97	51 (10)
para-xylene	D 5136	0.866	138–139	70	81 (27)	93	52 (11)
Ethylbenzene	D 3193	0.872	136–137	74	70 (21)	95	52 (11)
High flash aromatic naphthas	D 3734						
Type I "Aromatic 100"		0.874	150–175	20	108 (42)	91	56 (13)
Type II "Aromatic 150"		0.895	180–215	5	150 (66)	95	60 (15)

Naphthenic Hydrocarbons

Most of the aliphatic hydrocarbon solvents contain minor amounts of naphthenes, i.e., cycloparaffins, cyclic aliphatics. Properties of naphthenes, with respect to solvency, odor, and specific gravity, are intermediate between aliphatics and aromatics.

Purely naphthenic hydrocarbon solvents currently have very limited commercial availability. Cyclohexane, a pure naphthenic hydrocarbon, finds applications not as a solvent but as a chemical intermediate in the manufacture of nylon fiber and engineering resins, plasticizers, polyurethane, polyester, and epoxy resins. Properties are summarized in Table 3.

Terpenes

Terpene solvents are obtained from pine trees and to a much lesser extent as a by-product of the citrus industry. They are the oldest solvents used in coatings, predating ancient Egyptian civilization [*1,3*]. The main solvents in this group are turpentine, dipentene, and pine oil. Chemically, they are mixtures of C_{10} unsaturated hydrocarbon compounds. A good review of terpenes may be found in ASTM D 804, "Standard Definitions of Terms Relating to Naval Stores and Related Products."

Terpene solvents have volatiles similar to mineral spirits. However, they have only minor commercial significance today because they are more expensive than hydrocarbon solvents. Although their solvency is greater than that of aliphatic hydrocarbons, they have a much narrower range of solvency and evaporation rate and a stronger odor. Furthermore, because of their unsaturated structure, they are restricted in some areas by air pollution regulations.

There are four kinds of *turpentine*, as specified in ASTM D 13, Specification for Spirits of Turpentine, depending on the source and method of production [*1,4*].

Gum turpentine or *gum spirits* is produced by distilling the crude gum or oleoresin collected from living pine trees. It contains mostly α-pinene with lesser quantities of β-pinene and small amounts of other terpene hydrocarbons.

Steam-distilled wood turpentine is obtained from oleoresin within the wood of pine stumps or cuttings, either by direct steaming of the mechanically disintegrated wood or after solvent extraction of the oleoresin from the wood. It consists primarily of α-pinene, with small quantities of dipentene and other terpenes.

Sulfate wood turpentine is recovered during the conversion of wood to pulp by the sulfate (Kraft) paper-making process. It is a mixture of α- and β-pinene, with small amounts of other terpene hydrocarbons.

Destructively distilled wood turpentine is obtained by fractionation of certain oils recovered from the destructive distillation of pine wood. It is a complex mixture of a wide variety of aromatic hydrocarbons with only moderate quantities of terpenes being present.

Standard methods of sampling and testing turpentine are described in ASTM D 233, Methods of Sampling and Testing Turpentine.

Dipentene is obtained by fractional distillation from crude oils recovered in the several commercial methods of processing pine wood during the production of turpentine. It has somewhat stronger solvency and slower evaporation rate than turpentine. Standard test methods for sampling and testing dipentene are described in ASTM D 801, Methods of Sampling and Testing Dipentene.

Pine oil is a unique material separated during the four commercial turpentine production methods. Unlike the other hydrocarbon solvents, pine oil consists mainly of terpene alcohols, with a variety of small quantities of other oxygenated terpenes. Pine oil has strong solvent power due to the oxygen functionality. However, its evaporation rate is very slow. Pine oil is generally used in additive quantities, i.e., 5 wt% of the total solvent, to provide good coating flow out and wetting properties. Standard methods for sampling and testing pine oil are described in ASTM D 802.

d-Limonene is a relatively new commercial terpene hydrocarbon solvent recovered and purified from by-products of the citrus industry.

Typical properties of some selected terpene solvents are summarized in Table 4 [*5,6*].

TABLE 3—Typical properties of cyclohexane.

ASTM specification	D 3055
Specific gravity, 60/60°F	0.782
Distillation range, °C	174–178
Evaporation rate, *n*-butyl acetate = 100	1000 (estimated)
Flash point, °F (°C)	−4 (−20)
Kauri-butanol value	52
Aniline point, °F (°C)	93 (34)

Oxygenated Solvents

Oxygenated solvents contain oxygen functionality in the molecules. Unlike hydrocarbon solvents, oxygenated solvents

TABLE 4—Typical properties of selected terpene solvents.

	Wood Turpentine	Dipentene	Pine Oil
ASTM specification	D 13	...	...
ASTM test method	D 233	D 801	D 802
Specific gravity, 60/60°F	0.865	0.853	0.923
Distillation range, °C	150–170	170–190	200–225
Evaporation rate, *n*-butyl acetate = 100	40	18	5
Flash point, TCC, °F (°C)	95 (35)	120 (49)	130 (54)
Kauri-butanol value	56	62	>500
Aniline point, °F (°C)	70 (21)	32 (0)	<−4 (<−20)

are synthetically produced. Therefore, they are somewhat higher in cost. Most are pure, single-component chemical products, compared with hydrocarbon solvents which tend to be complex mixtures. Consequently, oxygenated solvents have very narrow distillation ranges, some as narrow as 1°C.

Relative to the hydrocarbons, oxygenated solvents have much stronger solvency and are used as active solvents for most synthetic resins. Their strong solvency, together with the wide range of volatilites available, makes them an extremely important group of solvents for the coatings industry. Other distinguishing characteristics include higher specific gravity and partial to complete water solubility.

There are four principal types of oxygenated solvents widely used in coatings: ketones, esters, glycol ethers (ether alcohols), and alcohols. Through blending, almost any desired combination of performance properties can be obtained.

Ketones

Ketones are characterized chemically by a carbonyl group bonded to two carbon atoms or alkyl groups in the molecule. This versatile class of solvents has powerful solvency and a wide range of evaporation rates, from very fast-evaporating acetone to slow-evaporating isophorone. Ketones are further characterized by their strong, sharp odors. They have narrow distillation ranges because of their high purity. Acetone is completely water miscible, while other ketones have varying degrees of water solubility. Properties of selected ketones, with their ASTM specification references, are summarized in Table 5. (Diacetone alcohol is included in this category since this ketone alcohol functions more as a ketone than an alcohol.)

Acetone is very fast-evaporating. It is often used in aerosols and sprayed coatings, particularly in nitrocellulose and acrylic lacquers, to effectively reduce viscosity for spray application and then quickly flash off during the spraying process. Methyl ethyl ketone (MEK) has a fast evaporation rate and methyl isobutyl ketone (MIBK) a moderate evaporation rate. They are extensively used as active solvents in synthetic resin lacquers and paints. The very slow evaporation rate of isophorone makes it useful in baked industrial coatings.

Esters

Esters used as solvents are alkyl acetates and propionates and glycol ether acetates. Several other types of ester solvents are also commercially available as specialty products. The alkyl esters cover a wide range of volatilities, mainly methyl through hexyl esters. Glycol ether acetates are slow-evaporating, and they are used as retarder solvents in solvent-based coatings and as coalescents in latex paints.

Esters have strong solvency, although generally slightly weaker than ketones of similar volatility. They are characterized by their pleasant, sweet, fruity odors. All esters have narrow distillation ranges since they are relatively pure compounds.

Typical properties of the most common ester solvents are summarized in Table 6. As with ketones, their solvencies follow a general pattern, diminishing with increasing molecular weight and with increasing branching of the molecule. Evaporation rate also decreases with increasing molecular weight, but increases with increased branching. *n*-Butyl acetate, one of the most important ester solvents, has a medium evaporation rate. It is used as a reference for expressing evaporation rates of other solvents.

Glycol Ethers

Glycol ethers are ether alcohols, having both ether and alcohol functionality. The ethylene glycol ethers, derived from ethylene oxide and alcohols, have been widely used in coatings. However, because of health hazard concerns associated with certain ethylene glycol ethers, they are being replaced in many applications by propylene glycol ethers which are derived from propylene oxide.

Glycol ethers have a truly unique combination of properties: strong solvency, slow evaporation rate, complete water miscibility, high flash point, and mild odor. They are often

TABLE 5—Typical properties of selected ketone solvents.

Solvent	ASTM Specification	Purity Test, ASTM	Specific Gravity, 20/20°C	Boiling Point, °C	Evaporation Rate, *n*-BuAc = 100	Flash Point, TCC, °F (°C)	Toluene Dilution Ratio
Acetone	D 329	D 1363	0.792	56	1160	0 (−18)	4.5
Methyl ethyl ketone	D 740	D 2804	0.806	80	570	20 (−7)	4.3
Methyl isobutyl ketone	D 1153	D 3329	0.802	116	165	60 (16)	3.6
Methyl isoamyl ketone	D 2917	D 3893	0.814	145	50	96 (36)	4.1
Methyl *n*-amyl ketone	D 4360	D 3893	0.817	151	40	102 (39)	3.9
Diacetone alcohol	D 2627	...	0.940	170	12	120 (49)	3.0
Isophorone	D 2916	D 2192	0.922	215	3	180 (82)	6.2

TABLE 6—Typical properties of selected ester solvents.

Solvent	ASTM Specification	Purity Test, ASTM	Specific Gravity, 20/20°C	Boiling Point, °C	Evaporation Rate, *n*-BuAc = 100	Flash Point, TCC, °F (°C)	Toluene Dilution Ratio
Methyl acetate	...	...	0.904	55	1180	0 (−18)	2.9
Ethyl acetate	D 4614[a]	D 3545	0.901	77	410	24 (−4)	3.1
Isopropyl acetate	D 3131	D 3545	0.873	88	360	35 (+2)	3.0
n-propyl acetate	D 3130	D 3545	0.889	101	230	55 (13)	3.2
Isobutyl acetate	D 1718	D 3545	0.871	115	145	62 (17)	2.7
n-butyl acetate	D 4615[a]	D 3545	0.883	126	100	81 (27)	2.8
n-amyl acetate	D 3540	D 1617	0.876	140	40	101 (38)	2.3
Methyl amyl acetate	D 2634	D 1617	0.858	148	20	96 (36)	1.7
n-hexyl acetate	D 5137	D 1617	0.874	165	17	134 (57)	1.8
n-butyl propionate	...	...	0.876	145	45	100 (38)	2.1
n-pentyl propionate	...	...	0.872	168	18	135 (57)	1.8
2-ethoxyethyl acetate[b]	D 3728	D 3545	0.974	156	20	126 (52)	2.5
PM acetate[c]	D 4835	D 4773	0.969	146	34	114 (46)	2.6

[a]Four grades.
[b]Ethylene glycol monoethyl ether acetate.
[c]Propylene glycol monomethyl ether acetate.

used in small percentages in lacquers and lacquer thinners as retarder solvents to maintain coating flow and leveling after most of the other solvents have evaporated. In these applications, their water miscibility is beneficial in reducing moisture blush. Glycol ethers are also widely used as coupling solvents in water-based coatings to solubilize the water-reducible polymers.

Chemical terminology for the glycol ethers is cumbersome. For example, 2-ethoxyethanol is also referred to as ethylene glycol monoethyl ether. Therefore, they are often identified by their commercial brand names. Typical properties of selected glycol ethers are summarized in Table 7.

Alcohols

Alcohols are chemically characterized as organic compounds having a single hydroxyl group. This structure imparts some degree of water solubility to alcohols, complete for the lower members, methanol, ethanol, and propanol, and partial for the higher members of the family. Alcohols are further characterized physically as having mild, pleasant odors. Typical properties of selected alcohols are summarized in Table 8.

By themselves, alcohols are very poor solvents or nonsolvents for most polymers. There are few exceptions; ethanol is a solvent for shellac, poly(vinyl acetate), poly(vinyl butyrate), some phenolics, and natural resins. Alcohols find applications as latent solvents or co-solvents for nitrocellulose lacquers, melamine-formaldehyde and urea formaldehyde resins, and certain alkyds. They are also useful coupling solvents, with glycol ethers, to solubilize water-reducible resins. In addition to their use as solvents, latent solvents, and coupling solvents, alcohols are used as chemical raw materials for the manufacture of other solvents (e.g., ketones and esters), monomers, and synthetic polymers.

Methanol is the fastest evaporating alcohol. It is the only alcohol which has some solvency for nitrocellulose. Methanol, historically known as wood alcohol, is now rarely used as a solvent because of its relative toxicity.

Pure ethyl alcohol (ethanol) is restricted in use by law to beverages and to scientific and analytical purposes. It cannot be used without a federal government permit. Commercial ethyl alcohol, for solvent and chemical intermediate use, is denatured with any of a large number of government-approved substances to make it unfit for use in beverages. There are close to 100 approved denatured formulations available in both 95 vol% (190 proof) and anhydrous (200 proof) grades. Because of the large multiplicity of grades, ASTM specifications have not been established for ethyl alcohol. Isopropyl alcohol can replace ethyl alcohol in most coating solvent applications.

Butyl alcohols (butanols) differ in volatility and solvency among the four isomers, which are: normal, secondary, iso-, and tertiary. All have moderate volatility. Branching increases volatility and decreases solvency. *n*-Butanol is by far the most widely used isomer. *t*-Butanol is a solid at room temperature.

TABLE 7—Typical properties of selected glycol ether solvents.

Solvent	ASTM Specification	Purity Test, ASTM	Specific Gravity, 20/20°C	Boiling Point, °C	Evaporation Rate, *n*-BuAc = 100	Flash Point, TCC, °F (°C)	Toluene Dilution Ratio
2-Methoxyethanol[a]	D 3128	...	0.966	125	56	103 (39)	4.0
2-Ethoxyethanol[b]	D 331	...	0.931	136	35	108 (42)	4.9
2-Butoxyethanol[c]	D 330	...	0.902	171	6	150 (66)	3.5
Propylene glycol monomethyl ether	D 4837	D 4773	0.923	121	71	94 (34)	5.2
Dipropylene glycol monomethyl ether	D 4836	D 4773	0.956	188	3	167 (75)	4.2

[a]Ethylene glycol monomethyl ether.
[b]Ethylene glycol monoethyl ether.
[c]Ethylene glycol monobutyl ether.

TABLE 8—Typical properties of selected alcohol solvents.

Solvent	ASTM Specification	Purity Test, ASTM	Specific Gravity, 20/20°C	Boiling Point, °C	Evaporation Rate, *n*-BuAc = 100	Flash Point, TCC, °F (°C)	Solubility, 20°C, wt%	
							In Water	Water In
Methanol	D 1152	E 346	0.793	64	600	52 (11)	Complete	Complete
Ethanol (anhydrous)	...	...	0.790	78	260	55 (13)	Complete	Complete
Isopropanol	D 770	...[a]	0.786	82	230	54 (12)	Complete	Complete
n-Propanol	D 3622	...[a]	0.804	97	100	74 (23)	Complete	Complete
sec-butanol	D 1007	...[a]	0.808	99	120	74 (23)	20.0	36.3
Isobutanol	D 1719	...[a]	0.803	107	70	85 (29)	9.5	14.3
n-butanol	D 304	...[a]	0.811	117	50	97 (36)	7.9	20.8
n-amyl alcohol	D 319	...[a]	0.813	130	30	91 (33)	1.7	9.2
Methyl isobutyl carbinol	D 2635	...[a]	0.808	131	30	103 (39)	1.6	6.3
2-ethyl hexanol	D 1969	D 5008	0.834	182	<1	164 (73)	0.1	2.6

[a]Purity and identity of these pure compounds are determined by a combination of tests of specific gravity (ASTM D 268 or D 4052), boiling point, and distillation range (ASTM D 1078).

The higher-boiling alcohols are used in relatively small amounts in solvent blends, and they find applications mainly in baked industrial coatings.

Other Oxygenated Solvents

Specialty oxygenated solvents include furan solvents and organic carbonates. Currently, they are not specified by ASTM standards. Information about them may be obtained from their suppliers.

Furan solvents of commercial interest include furfuryl alcohol, tetrahydrofuran (THF), and tetrahydrofurfuryl alcohol. These solvents have a cyclic ether structure and are characterized by exceptionally strong solvency for some synthetic resins, especially vinyls.

Ethylene and propylene carbonates are cyclic organic esters which are good solvents for many organic and inorganic materials. The former is a solid at room temperature. Characteristics of these carbonates include high flash point, very slow evaporation rate, high specific gravity, and very low odor.

Other Solvents

Chlorinated Hydrocarbons

Chlorinated solvents obviously contain chlorine atoms in the molecules. This gives them unique features of non-flammability, i.e., no flash point, and very high specific gravity. Several chlorinated solvents specified by ASTM standards are summarized in Table 9.

Methylene chloride has long been the active ingredient in most paint removers. It has strong solvency to soften and swell cured paint films and a very fast evaporation rate.

1,1,1-trichloroethane (methylchloroform) has found solvent applications in coating formulations because it is considered to be non-photochemically reactive by many regulatory agencies, and therefore it does not have to be included in measuring volatile organic compound (VOC) content [*1*].

Trichloroethylene is widely used for metal cleaning in vapor degreasing operations. (See ASTM D 3698, Practice for Solvent Vapor Degreasing Operations.)

Use of chlorinated solvents is declining due to (a) global concerns about their damaging effects on the earth's protective ozone layer and (b) concerns about the toxicity and carcinogenicity of many chlorinated solvents.

Nitrated Hydrocarbons

Nitrogen-containing hydrocarbon solvents include nitroparaffins and N-methyl-2-pyrrolidone (NMP). These are not currently specified by ASTM standards.

There are four nitroparaffinic solvents commercially available: nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane (2NP). Of these, 2NP is of most interest to the coatings industry. It has an evaporation rate similar to that of *n*-butyl acetate, and it is reported to have fast solvent release from coating films.

NMP is a specialty solvent having strong solvency, high flash point, complete water solubility, and high specific gravity. It is reported to be biodegradable and have a low order of toxicity. Applications include paint strippers, water-based coatings, printing inks, and reaction solvent for high-temperature resins.

TABLE 9—Typical properties of selected chlorinated hydrocarbon solvents.

Solvent	ASTM Specification	Grade or Application	Specific Gravity, 20/20°C	Boiling Point, °C	Evaporation Rate, *n*-BuAc = 100
Methylene chloride	D 3506	Pentachlorophenol solutions	1.366	39	1450
	D 4079	Vapor degreasing			
	D 4701	Technical grade			
1,1,1-trichloroethane	D 4126	General solvent; vapor degreasing	1.327	72	600
Trichloroethylene	D 4080	Vapor degreasing	1.465	86	450
Perchloroethylene	D 4081	Drycleaning	1.625	121	210

Supercritical Carbon Dioxide [7]

It has long been known that certain gases under supercritical temperature and pressure conditions can behave as solvents. They have become useful in a variety of industrial and analytical separation processes, such as extraction, polymer fractionation, chromatography, and catalyst regeneration, and as a reaction medium.

Supercritical fluids have properties intermediate to those of normal liquids and gases. The supercritical fluid region on a phase diagram corresponds to temperatures and pressures near or above the critical point of the fluid where the properties of the liquid and gas are similar or identical, so that in effect only one fluid phase, which is simultaneously liquid-like and gas-like, exists (Fig. 1).

Supercritical carbon dioxide has many useful attributes which make it attractive as a diluent for spray-applied coatings. Carbon dioxide is environmentally compatible because it is not regarded as a volatile organic compound (VOC). It acts as a hydrocarbon diluent and replaces organic solvents to the extent of 10 to 30 vol% of a formulation. Low VOC coatings can be formulated with existing high-performance polymer systems, and 70 to 80% reductions in VOC are achievable. Using carbon dioxide as a coating solvent effects a net reduction in the amount of "green house" carbon dioxide that is otherwise produced as a result of coating operations.

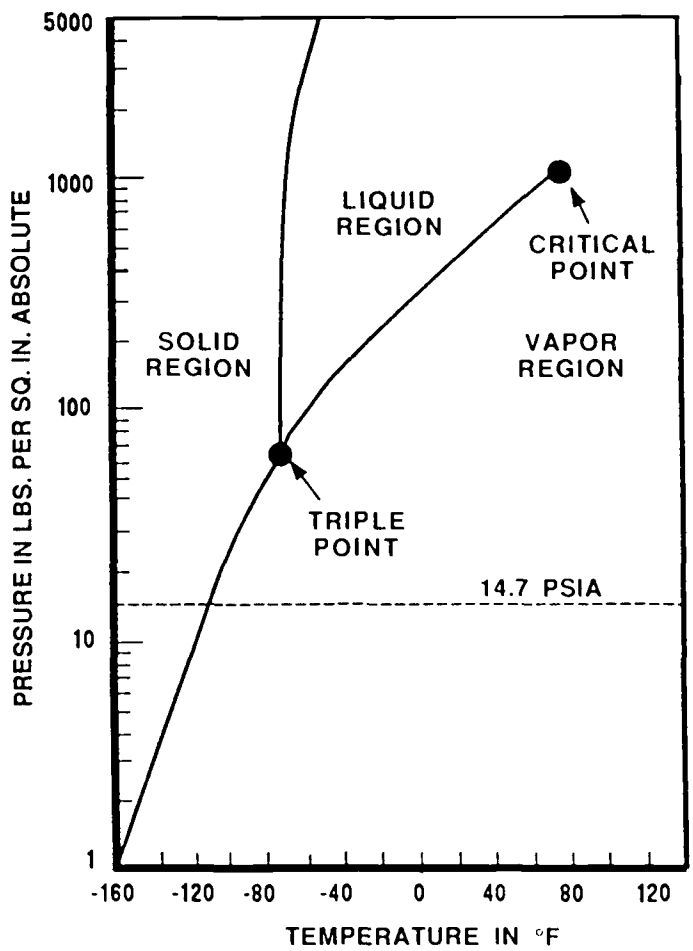

FIG. 1—Phase diagram for carbon dioxide [7].

The UNICARB®[2] process has been developed to utilize supercritical carbon dioxide in airless sprayed coating operations. It has numerous advantages in this application. The temperatures and pressures necessary to use supercritical carbon dioxide are well within the capabilities of present hot, airless spray systems.

Carbon dioxide has low toxicity, is non-flammable, inert, inexpensive, and readily available. Supercritical carbon dioxide has high solubility in most coating formulations, and it is a good viscosity reducer for polymer solutions. In the actual spraying process, it behaves as a highly volatile solvent, producing vigorous atomization that can remedy many of the defects of airless spraying, thereby achieving high quality coatings.

CLASSIFICATION BY FUNCTION

Solvents can be classified according to the function they perform in an end-use application: active solvents, latent solvents, and diluents.

Active Solvents

Active solvents are sometimes called "true solvents." They are the ones that really do the work to dissolve resins and other film formers. Active solvents are usually the more expensive ones with strong solvent power: ketones, esters, and glycol ethers. They are essential for dissolving film-forming resins and for effectively reducing viscosities of paints, varnishes, and lacquers for application.

Relative solvency of active solvents, particularly for lacquers, may be determined by ASTM method D 1720, Dilution Ratio of Active Solvents in Cellulose Nitrate Solution, and expressed in terms of toluene dilution ratio. Stronger solvents will tolerate more hydrocarbon diluent and still keep resins in solution. High toluene dilution ratio values indicate strong solvency. Typical values for selected active solvents may be compared in Tables 5 through 7.

Latent Solvents

By themselves, latent solvents are either poor solvents or nonsolvents for most coating resins. However, they possess a hidden or latent solvency which manifests itself when they are used in combination with active solvents. Latent solvents then behave as if they were strong active solvents. This synergism is used to advantage in formulating nitrocellulose lacquers in particular. Latent solvents are often alcohols, and they are intermediate in cost.

Diluents

Diluents are generally nonsolvents if used alone with synthetic resins. Their function is to participate in solvent blends to provide viscosity reduction through dilution of lacquers and paints and to reduce the cost of thinners and coating

[2]Union Carbide Chemicals and Plastics Co. Inc., 39 Old Ridgebury Road, Danbury, CT 06817-0001.

solvent blends. Diluents are usually low-cost hydrocarbon solvents.

There is usually a limit to how much diluent will be tolerated by coating resins in a solvent blend. If the limit is exceeded, the resins will start to gel or precipitate from solution. Aromatic hydrocarbon solvents are usually tolerated in greater amounts than are aliphatic hydrocarbons.

ASTM Method D 1720 may be used to determine the relative tolerances for hydrocarbon diluent when *n*-butyl acetate is used as the reference active solvent. In the test, the maximum ratio of hydrocarbon diluent to *n*-butyl acetate that will be tolerated by a solution of 8 g of nitrocellulose in a total of 100 mL of solvent and diluent is determined. This provides a measure of the suitability of the diluent for lacquer solvent formulations. For example, the toluene dilution ratio of *n*-butyl acetate is 2.8, while the VM&P naphtha dilution ratio is only 1.2, indicating a much greater tolerance for toluene than for VM&P naphtha.

Solvent Balance

In formulating coating solvents and thinners, careful attention must be paid to the proper balance of solvency and evaporation rate. Generally, expensive active solvents are kept to a minimum amount sufficient to provide adequate solvency and viscosity reduction. Diluent content is usually maximized to keep cost low.

Evaporation rate of each component must be considered in selecting appropriate active solvents and diluents depending on the method of coating application. As the applied coatings dry, the balance of active solvents and diluents remaining in the wet coating must be such that solvency for the coating resin remains sufficiently strong throughout the drying process. Otherwise, resin blush, i.e., precipitation or separation of the resin, can occur resulting in loss of gloss, incompatibility, haze, or other serious coating defects.

KEY PERFORMANCE REQUIREMENTS

Solvency

Solvency is the foremost performance requirement of a solvent. From a practical perspective, the term "solvency" to a coatings formulator refers to the ability of a solvent to (a) dissolve resins, (b) hold those resins in solution in the presence of diluents, and (c) efficiently reduce viscosity of resin solutions, lacquers, and paints. In general, relative solvency is measured indirectly by determining compatibility of specified resins or a chemical reagent with the solvent under test.

Three test methods are most often used for measuring and expressing relative solvent strength: kauri-butanol value, aniline point, and diluent dilution ratio. The first two test methods are used exclusively for hydrocarbon solvents and the latter test for only oxygenated solvents. Although these methods are somewhat archaic, the values obtained have been found to be useful in estimating general solvency for many coating resins.

Another method, a viscosity reduction test, provides a means of direct measurement of solvent power when a specific resin under consideration is employed. Solvents are directly compared by measuring the viscosities of solutions at different resin concentrations and plotting viscosity versus resin concentration.

Kauri-Butanol Value

Kauri-butanol value (KBV) is one measure of the solvent power of hydrocarbon solvents. High KBV indicates relatively strong solvency and often relatively high aromatics content as well. Typical KBVs may be compared in Tables 1 through 4.

KBV is a continuous scale and is sometimes used as an indicator of aromatics content; low aromatic (aliphatic) hydrocarbons have low KBVs and weak solvency, while highly aromatic hydrocarbons have high KBVs and relatively strong solvency. For example, odorless mineral spirits at the low end of the scale has a KBV of about 27, regular mineral spirits about 37, and aromatic hydrocarbons close to 100.

KBV is defined in ASTM Method D 1133, Kauri-Butanol Value of Hydrocarbon Solvents, as the volume in milliliters of the solvent at 25°C required to produce a defined degree of turbidity when titrated into a specified quantity of a standard clear solution of kauri resin in *n*-butyl alcohol. Kauri resin, a natural product, now archaic, was once used as a coating resin. However, standard test solutions are available from chemical supply companies. The kauri resin solution is standardized against toluene, which has an assigned value of 105, and a mixture of 75% *n*-heptane and 25% toluene on a volume basis, which has an assigned value of 40.

The procedure is to accurately weigh 20 g of standardized kauri-butanol solution into an Erlenmeyer flask and bring the flask and its contents to 25°C in a water bath. It is then titrated with the solvent being tested to a turbidity end point that occurs when the sharp outlines of 10-point print on a sheet placed under the flask are obscured or blurred but are not illegible. Turbidity at the end point is caused by precipitation of the kauri resin at incipient incompatibility.

This test is not applicable to oxygenated solvents.

Aniline Point

Aniline point (or mixed aniline point) is another measure of solvency of hydrocarbon solvents. In addition, it is often used to provide an estimate of the aromatics content of hydrocarbon mixtures. Aromatic hydrocarbons (strong solvents) exhibit the lowest aniline points and aliphatics (weak solvents) the highest. Naphthenes have values between those for aromatics and aliphatics. In homologous series, the aniline point increases with increasing molecular weight, i.e., decreasing solvency.

Aniline point is defined in ASTM Method D 611, Aniline Point and Mixed Aniline Point of Petroleum Products and Hydrocarbon Solvents, as the minimum equilibrium solution temperature for equal volumes of aniline and solvent. The reagent for this test is aniline, a clear liquid at room temperature. The procedure requires that equal volumes of aniline and hydrocarbon solvent are placed in a jacketed tube and mechanically mixed. The basic apparatus is shown in Fig. 2, although ASTM D 611 also describes alternative variations in the manual apparatus and an automatic apparatus as well.

Hydrocarbon solvents containing less than 50% aromatics will generally form an incompatible, turbid mixture at room temperature [*8*]. Therefore, the stirred mixture is heated at a

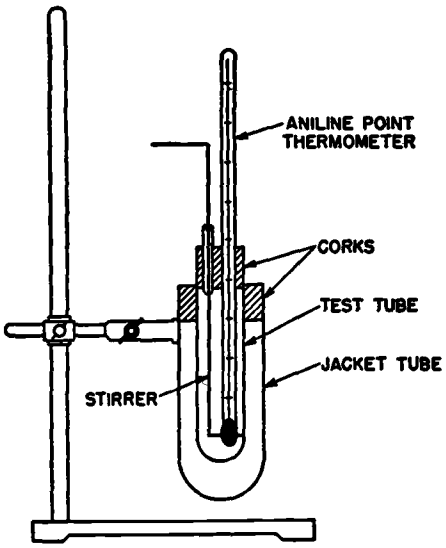

FIG. 2–Aniline point apparatus.

controlled rate until the two phases become miscible and clear. The stirred mixture is then allowed to cool at a controlled rate until it suddenly becomes cloudy throughout. The temperature at this end point is recorded as the aniline point of the solvent.

Hydrocarbon solvents containing more than 50% aromatics will generally form clear, miscible solutions with aniline at room temperature [*8*]. When this occurs, the stirred mixture must be cooled below room temperature at a controlled rate until the cloudy transition point suddenly appears. The temperature at this cloud point is the aniline point.

With hydrocarbons having high aromatics content, the aniline point may be far below room temperature and below the temperature at which aniline will crystallize from the aniline-sample mixture. To treat this circumstance, it becomes necessary to perform a "mixed aniline point" test. Instead of using equal volumes of aniline and sample, a mixture containing two volumes of aniline, one volume of sample, and one volume of *n*-heptane of specified purity is made. The test is then performed as described above, and the result is reported as the "mixed aniline point." Again, low values indicate strong solvency (the opposite of kauri-butanol values).

Unlike the continuous KBV scale, a disadvantage of the aniline point and mixed aniline point is that the two scales are not continuous. Therefore, it is difficult to directly compare high- and low-aromatic content solvents [*8*].

This test is not applicable to oxygenated solvents.

Diluent Dilution Ratio

The diluent dilution ratio test measures the solvency of oxygenated (active) solvents by determining their ability to hold in solution a difficult-to-dissolve resin, nitrocellulose, in the presence of hydrocarbon diluent. The test measures the maximum ratio of hydrocarbon diluent to oxygenated solvent that can be tolerated by the nitrocellulose solution. Strong oxygenated solvents provide a high tolerance for diluent and have high diluent dilution ratios. Typical values may be compared in Tables 5 through 7.

ASTM Method D 1720 defines diluent dilution ratio as the maximum number of unit volumes of a diluent that can be added to a unit volume of solvent to cause the first persistent heterogeneity (precipitation) in the solution at a concentration of 8 g of cellulose nitrate per 100 mL of combined solvent plus diluent at 25°C.

The procedure is to dissolve carefully dried nitrocellulose in the oxygenated (active) solvent, and with stirring, add hydrocarbon diluent by titration. The end point occurs at the first persistent appearance of resin precipitation or gelation. Additional active solvent is then added to redissolve the resin, and titration is continued to a second end point. The data are plotted to determine the ratio of diluent to active solvent at exactly 8 g of cellulose nitrate per 100 mL of total solvent.

Most often, toluene is used as the diluent in the test, and the result is expressed as the "toluene dilution ratio." However, other hydrocarbons, e.g., VM&P naphtha, may also be used, thereby producing different (lower) values expressed as "naphtha dilution ratios." Although cellulose nitrate is used as the "reagent" in this test, and the results are most meaningful for formulating nitrocellulose lacquers, it has been found from experience that the solvency ranking of oxygenated solvents according to their diluent dilution ratios applies to other coating resins as well.

As described in the Section entitled "Diluents," ASTM D 1720 may also be applied to compare and measure the suitability of specific diluents for use in lacquer solvent and thinner formulations by using *n*-butyl acetate as the reference active solvent in the test.

Dilution Limit

Some resins are soluble at high concentrations in a solvent but become incompatible and precipitate when diluted below a critical concentration, which is termed the dilution limit. Sometimes, this concentration is within the range of practical formulations. Therefore, it is important to know whether a dilution limit exists for a particular resin. To determine the dilution limit, a known weight of resin is dissolved in the solvent. Solvent is then added until precipitation, the first persistent cloudiness, appears. Dilution limit is expressed as the percent by weight of resin at the end point [*8*].

Viscosity Reduction

The relative solvency of different solvents for a given resin may be compared with each other or with a reference solvent by measuring the viscosities of different concentrations of the given resin in each of the solvents. The viscosities are then plotted as a function of resin concentration. An example is shown in Fig. 3 [*1*].

Viscosities of resin solutions can be measured precisely by ASTM Method D 445, Kinematic Viscosity of Transparent and Opaque Liquids, or by ASTM Method D 1725, Viscosity of Resin Solutions. A simpler, more widely used, but less precise method for determining resin solution viscosities is ASTM Method D 1545, Viscosity of Transparent Liquids by Bubble Time Method (Gardner-Holdt Viscosity).

At high resin concentrations, solution viscosity will depend on solvency of the solvent and solubility of the resin. However, at low resin concentrations, the solution viscosity becomes more influenced by viscosity of the pure (neat) solvent. Viscosities of selected solvents are listed in Table 10 [*17*].

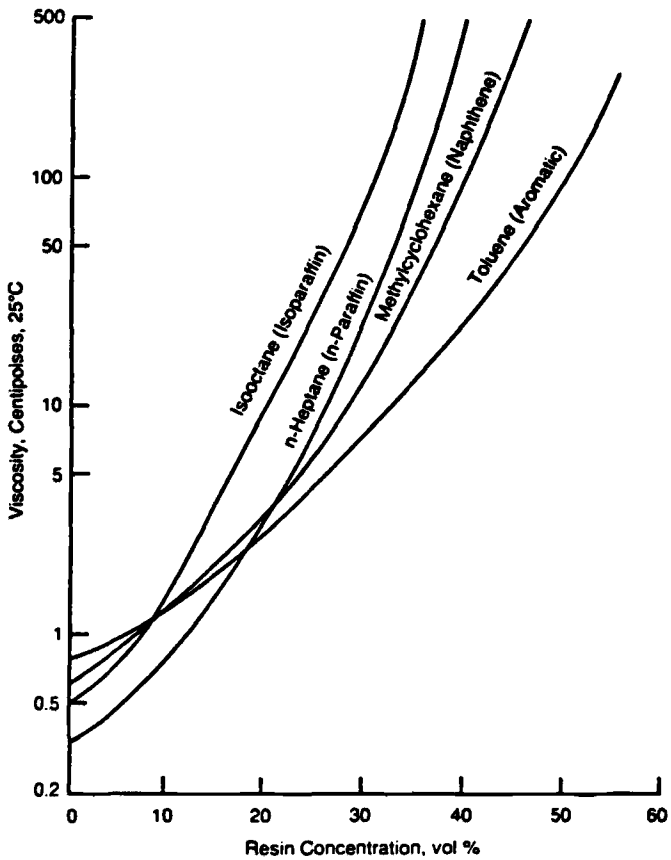

FIG. 3–Effect of solvent type on solution viscosity (medium oil alkyd in four hydrocarbon types) [*1*].

TABLE 10—Viscosities of typical commercial solvents.

Solvent	Viscosity, Cp at 25°C
Hydrocarbons	
VM&P naphtha	0.68
Mineral spirits	1.10
Toluene	0.62
Xylene	0.67
High-flash aromatic naphtha	1.08
Ketones	
Acetone	0.31
Methyl ethyl ketone	0.41
Methyl isobutyl ketone	0.56
Methyl isoamyl ketone	0.73
Methyl amyl ketone	0.77
Isophorone	2.3
Esters	
Ethyl acetate	0.45
Isopropyl acetate	0.52
Isobutyl acetate	0.68
n-butyl acetate	0.68
n-amyl acetate	0.83
Propylene glycol monomethyl ether acetate	1.1
Ethylene glycol monoethyl ether acetate	1.2
Ethylene glycol monobutyl ether acetate	1.7
Alcohols	
Ethanol	1.1
n-propanol	2.0
i-propanol	2.4
n-butanol	2.6
s-butanol	2.9
n-amyl alcohol	3.7
Glycol Ethers	
Propylene glycol monomethyl ether	1.7
Ethylene glycol monoethyl ether	1.9
Ethylene glycol monobutyl ether	2.9

Solubility Parameters

Great strides have been made in developing theoretical models to describe solvency and to predict the capacity of a pure solvent or solvent blend to dissolve a given resin. The concept of solubility parameters was first proposed by Hildebrand [*9,10*], and it was applied to practical applications in the coatings industry by Burrell [*11*]. Further refinements and enhancements to the solvency model made by Burrell [*12*], Crowley [*13*], Hansen [*14,15*], and others have resulted in the evolution of a model that is workable, reasonably accurate in its predictions, and useful as a formulating tool.

The three-dimensional solubility parameter is the most widely used method for predicting miscibility/solvency between solvents and polymers. In this method, each polymer and each solvent is characterized by three solubility parameters: δ_d representing dispersion forces, δ_p representing polar forces, and δ_h representing hydrogen bonding forces. Therefore, polymers and solvents can be represented by points in a three-dimensional plot using the three solubility parameters.

Each polymer point may constitute the center of a sphere, the so-called "sphere of solubility," of radius R, known as the radius of interaction. Solvents whose points lie at a distance less than R from the center of the polymer's sphere, i.e., within the sphere, should dissolve the polymer. Conversely, solvents whose point coordinates lie outside of the sphere are not expected to dissolve the polymer [*16*]. A more thorough discussion of solubility parameters can be found in Chapter 35.

A very comprehensive source of solubility parameter information and data is the "CRC Handbook of Solubility Parameters and Other Cohesive Parameters" by A. F. M. Barton (CRC Press, 1983). A simpler, two-dimensional approach to solubility parameters, employing only the dispersion and hydrogen bonding parameters, is described in ASTM Method D 3132, Test for Solubility Range of Resins and Polymers. Most major solvent suppliers have developed computer programs, based on the solubility parameter concept, to aid in formulating solvent blends to optimize solvency, obtain desired performance requirements, and minimize cost.

Volatility

Volatility of a solvent describes its inherent tendency to transform from a liquid to a vapor. The fundamental controlling property is vapor pressure. Volatility is manifested by such properties as evaporation rate, boiling point, and flash point.

Vapor Pressure

All liquids have a tendency to vaporize and become gases, depending upon their relative vapor pressures. A solvent's

liquid vapor pressure is the pressure exerted by molecules at the liquid surface in their attempt to escape the liquid phase and penetrate their gaseous environment. In a physical sense, vapor pressure is the force exerted on the walls of a closed container by the vaporized portion of the liquid. Conversely, it is the force which must be exerted on the liquid to prevent it from vaporizing further. For a given liquid solvent, vapor pressure is a function purely of temperature. The more volatile a solvent, the higher the liquid vapor pressure at a specified temperature and the faster the vaporization, i.e., evaporation rate. A knowledge of the vapor pressure/temperature relationship is important in the safe design of solvent storage and distribution equipment to minimize solvent losses by vaporization.

Relative vapor pressures of pure solvents and blends are measured at 100°F (38°C) by ASTM Method D 323, Reid Vapor Pressure (RVP). The RVP apparatus consists of a double-chamber bomb fitted with a pressure gage. The lower chamber, which has one quarter the capacity of the upper chamber, is filled with the liquid solvent sample. The sample and its chamber are chilled to 0°C (32°F) to reduce premature evaporation, the bomb is sealed, and it is immersed in a 100°F (38°C) water bath. To assure full opportunity for vaporization, the bomb is removed from the bath periodically for a brief vigorous shaking. When an equilibrium temperature is reached and when the bomb pressure gage (which initially registered zero) has stabilized at maximum value, the pressure is recorded. After applying appropriate correction factors, the pressure is reported as Reid vapor pressure at 100°F (38°C).

Alternatively, vapor pressure of a solvent can be measured over a wide range of temperatures by ASTM Method D 2879, Vapor Pressure by Isoteniscope. This procedure utilizes a differential manometer, one leg of which is exposed to saturated vapor while the other is evacuated. Measurements are reported in absolute units. Absolute vapor pressures of selected solvents at 20°C are listed in Table 11 [*6,17*].

TABLE 11—Vapor pressures of typical commercial solvents.

Solvent	Vapor Pressure at 20°C, mm Hg
Hydrocarbons	
VM&P naphtha	5.2
Mineral spirits	3.4
Toluene	38
Xylene	9.5
High-flash aromatic naphtha	<1
Ketones	
Acetone	185
Methyl ethyl ketone	85
Methyl isobutyl ketone	16
Methyl isoamyl ketone	4.0
Methyl amyl ketone	1.0
Isophorone	0.3
Esters	
Ethyl acetate	76
Isopropyl acetate	48
Isobutyl acetate	12.5
n-butyl acetate	7.8
n-amyl acetate	4.0
Propylene glycol monomethyl ether acetate	3.7
Ethylene glycol monoethyl ether acetate	1.7
Ethylene glycol monobutyl ether acetate	0.29
Alcohols	
Ethanol	44
i-propanol	31
n-propanol	15
s-butanol	12
n-butanol	4.4
n-amyl alcohol	2.0
Glycol Ethers	
Propylene glycol monomethyl ether	11
Ethylene glycol monoethyl ether	4.1
Ethylene glycol monobutyl ether	0.9

Evaporation Rate

Evaporation rate of a solvent is second only to solvency in its importance to the coatings industry. Although solvents are transient ingredients of a coating, they perform vital functions but must ultimately leave the coating film by evaporation. During application of a coating, solvents play a role in controlling flow characteristics as the film forms. If solvent evaporation is too fast, the coating film will not level and flow out to form a smooth surface, the result being a rough, "orange peel" effect in spray-applied coatings, or brush marks if brush applied. Conversely, if solvent evaporation is too slow, the coating may run and sag on vertical surfaces, or solvents may become trapped in the film as it cures, thus impairing performance properties of the coating.

Proper solvent balance, the ratio of active solvent to diluent, is also important. If this balance becomes upset as a result of composition changes during evaporation, resin precipitation can occur, thereby causing a loss of film integrity. Therefore, solvent evaporation rate is a key factor in the formulation of coatings. Relative evaporation rates of selected solvents of various types may be compared in Fig. 4 and in Tables 1 through 9.

Evaporation rates of solvents are always expressed on a relative basis. They are not absolute values in practical situations because evaporation rates are dependent upon numerous environmental factors including temperature, airflow, humidity, exposed surface area, and the presence of resin and pigment. Humidity has no effect on the evaporation of hydrocarbon solvents, but it can significantly retard evaporation of oxygenated solvents which are completely or partially water miscible.

It is common practice to express evaporation rates relative to *n*-butyl acetate, a widely used, medium-evaporating solvent as a reference. Evaporation rate of *n*-butyl acetate is arbitrarily assigned a value of 100 (or sometimes 1.0 depending on the scale used). Solvents evaporating faster than *n*-butyl acetate have higher values for evaporation rate; those solvents evaporating slower have lower numerical values. Use of a reference standard compensates for differences in test procedure or environmental factors.

Numerous techniques have been used for measuring relative evaporation rates, some of them gravimetric, some volumetric. The ones currently most widely used are based on the gravimetric procedure and instrumentation (or some variation thereof) described in ASTM D 3539, Test Method for Evaporation Rates of Volatile Liquids by Shell Thin-Film Evaporometer. In this method, a measured volume of liquid

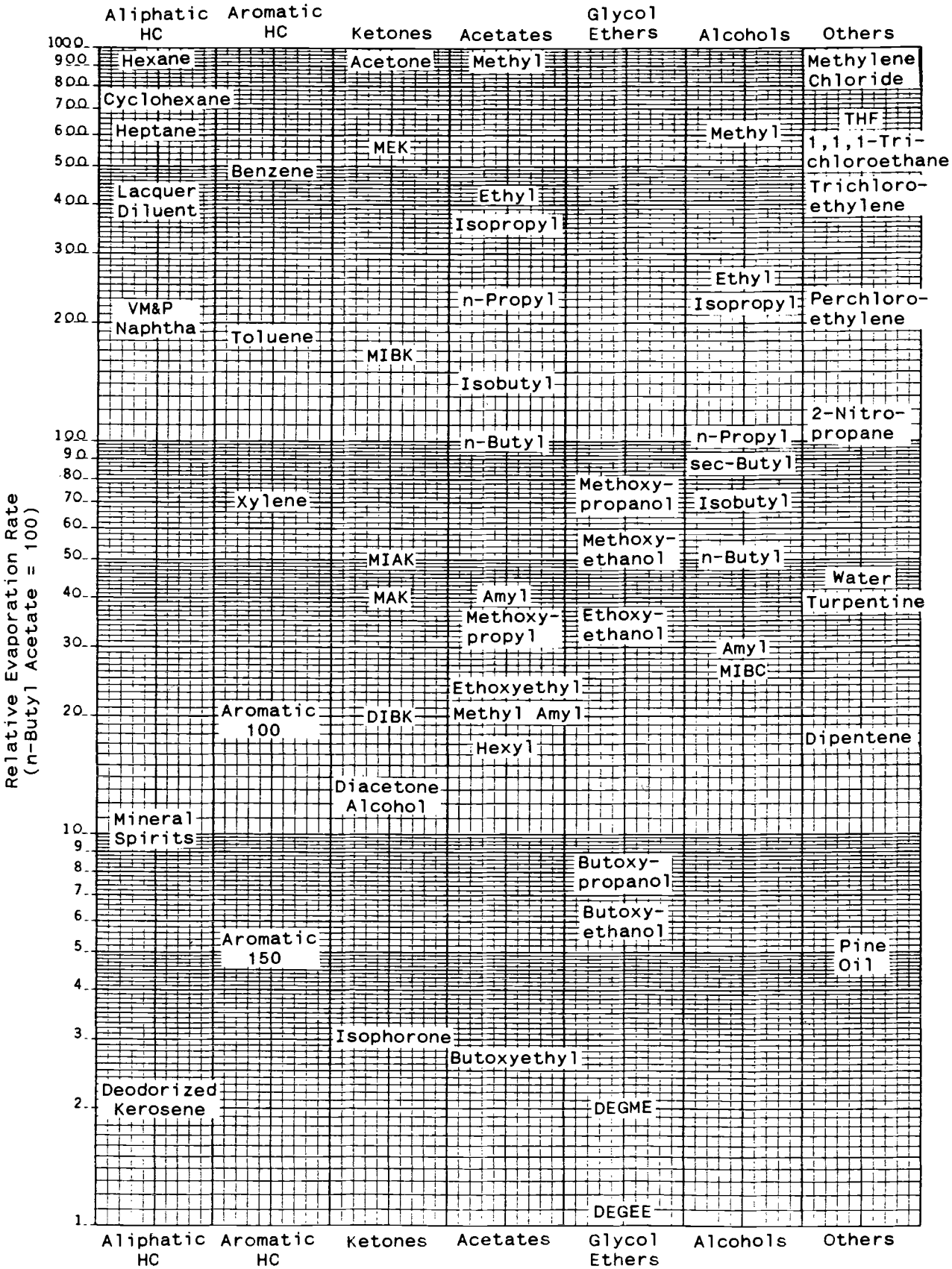

FIG. 4–Relative solvent evaporation rates.

solvent is spread on a known area of filter paper that is suspended from a sensitive balance in a controlled environment cabinet. Weight loss of the filter paper/solvent liquid is measured as a function of time as the solvent evaporates.

Early models of the apparatus use a Jolly spring as the gravimetric measuring device and require manual measurement of weight and time (Fig. 5). More recent models employ an electrobalance and automatically record weight loss versus time (Fig. 6). The Shell Thin-Film Evaporometer and the Chevron Research Evapograph operate under similar principles.

The basic procedure with both the manual and automatic instruments is similar. The evaporation chamber and sample are conditioned to 25°C (77°F). Airflow rate (21 L/min) and relative humidity (less than 5%) in the chamber are set. A filter paper, 90 mm in diameter, is horizontally suspended in the evaporation chamber from the weight-sensing device. The solvent sample (0.7 mL) is added from a hypodermic syringe and distributed over the entire area of the filter paper within a period of 10 s. Data are reported as time in seconds for 10% solvent weight increments through the evaporation cycle, and they are plotted as percent solvent evaporated versus elapsed time (for example, see Fig. 7) [*8,18*]).

The procedure is repeated using *n*-butyl acetate as the reference standard. Elapsed time for 90% evaporation of specimen and standard are determined. Evaporation *rate* of the solvent specimen is calculated as the ratio of 90% evaporation time for *n*-butyl acetate standard divided by the 90% evaporation time for the solvent specimen and normalized so that the evaporation rate of *n*-butyl acetate is 100 (or 1.0). The 90% evaporation time is generally used since some curvature of the plot usually occurs above that data point. Evaporation plots for pure solvents are nearly straight lines. Solvent mixtures or blends produce curved plots, the curvature becoming more extreme as differences in the evaporation rates of individual blend components become greater. Several solvent suppliers have developed computer programs to model and predict evaporation rates of solvent blends [*25–29*].

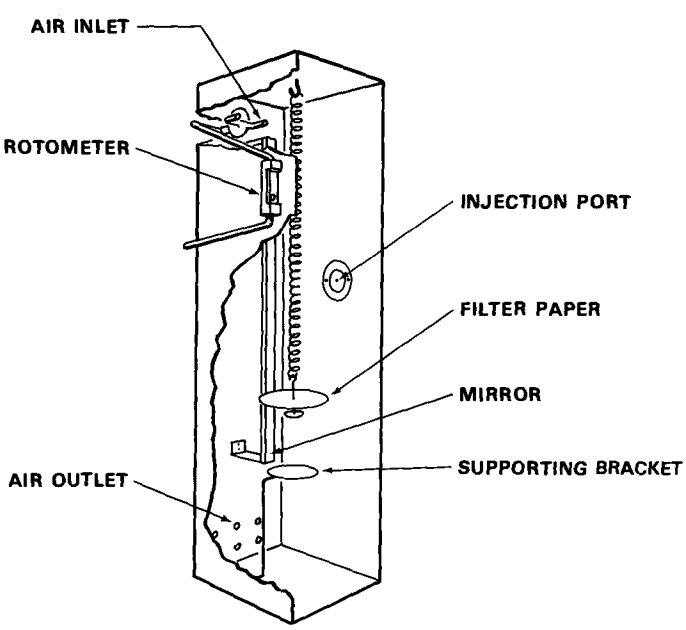

FIG. 5–Thin-film evaporometer.

The information presented so far has dealt with the evaporation of neat (pure) solvents. The presence of resin solute, e.g., in a lacquer or paint, retards solvent evaporation as illustrated in Fig. 8. In addition, some solvents are preferentially retained more than others by certain polymers due to solvent/polymer interactions arising from factors such as polarity and hydrogen bonding.

As solvent evaporation from a coating film progresses, it slows down markedly. The evaporation rate-limiting factor changes from neat solvent volatility to diffusion through the coating film. Diffusion-limited evaporation is much slower [*19*].

Actual evaporation of solvents from polymer films must be determined empirically. Although there are no standard test methods for doing so, various experimental procedures are reported in the literature [*8*]. Murdock and Wirkus [*20*], as well as Hays [*21*], tagged solvents with carbon-14 and measured residual radioactivity after the bulk of the solvent had evaporated. More recently, gas chromatography has been used effectively. Sletmoe modified a Shell thin-film evaporometer to permit sampling and subsequent analysis of evaporating vapor [*22*]. Lesnini evaporated the solvent from a series of solution aliquots and used a gas chromatograph to determine the type and amount of solvent remaining [*23*]. He dissolved the resin solution in a carrier solvent to ensure that a representative sample of the retained solvent was recovered for analysis.

A similar empirical procedure was used by a major solvent supplier to develop a database and appropriate algorithms for a solvency/evaporation rate computer program [*24,25*]. The program models solvency and evaporation rates of solvent blends from coating films, taking into account specific resin/solvent interactions. It calculates evaporation data for solvent blends evaporating from coating films and the compositions and solvency interaction radii of the solvent blends remaining in the film at any time.

Boiling Point/Distillation Range

Vapor pressure of a solvent increases as its temperature increases, as illustrated in the generalized graph in Fig. 9. If a solvent is heated to a high enough temperature, its vapor pressure will eventually rise to a value equal to 1 atm (e.g., 760 mm mercury pressure at sea level). At that point, the solvent will vaporize not only from the surface of the liquid, but vapor bubbles will form within the body of the liquid. This phenomenon is called "boiling," and the corresponding temperature at which it initially occurs is the "boiling point" [*30*]. When a solvent consists of a mixture of chemical components, as is the case with most hydrocarbon solvents, boiling occurs over a range of temperatures referred to as the "boiling range" or "distillation range." Single-component, pure solvents have single, unique boiling points or very narrow distillation ranges.

Distillation temperature or range is an important physical property which is listed in all solvent specifications. It is useful as an identification test (in combination with other tests, such as specific gravity), but will not differentiate between solvents of similar boiling point or range. Distillation range also gives an indication of solvent purity. This is partic-

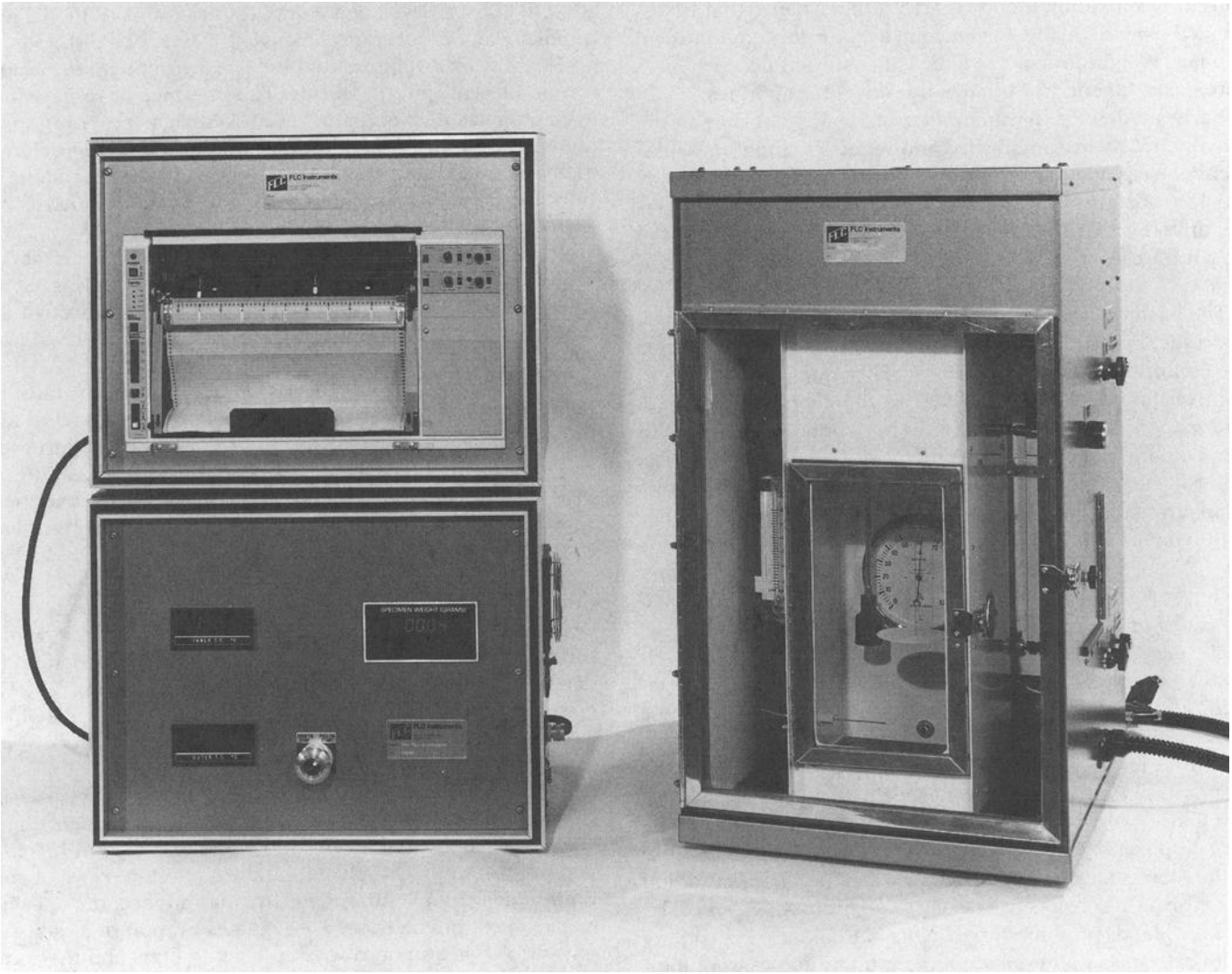

FIG. 6–Automatic thin-film evaporometer.

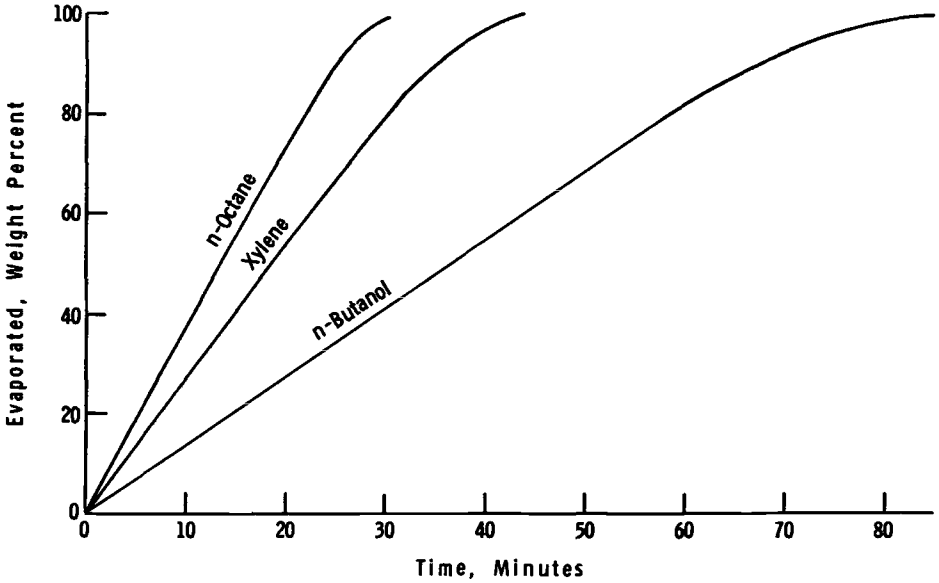

FIG. 7–Evaporation rates of typical solvents (Chevron Research Evapograph at 80°F).

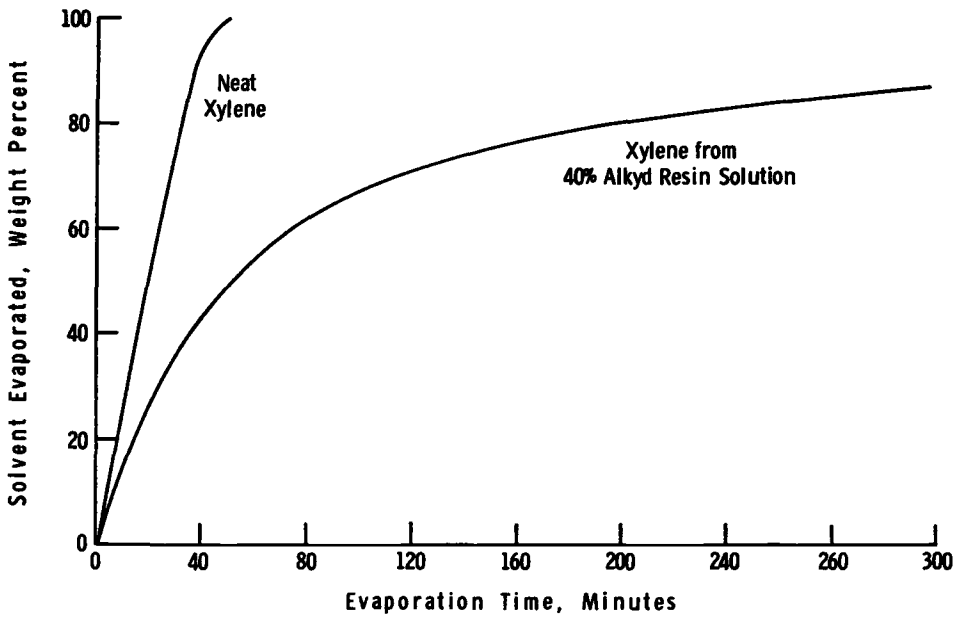

FIG. 8–Evaporation rate of xylene—Neat, and from a 40% solution of medium oil alkyd (Chevron Research Evapograph at 80°F).

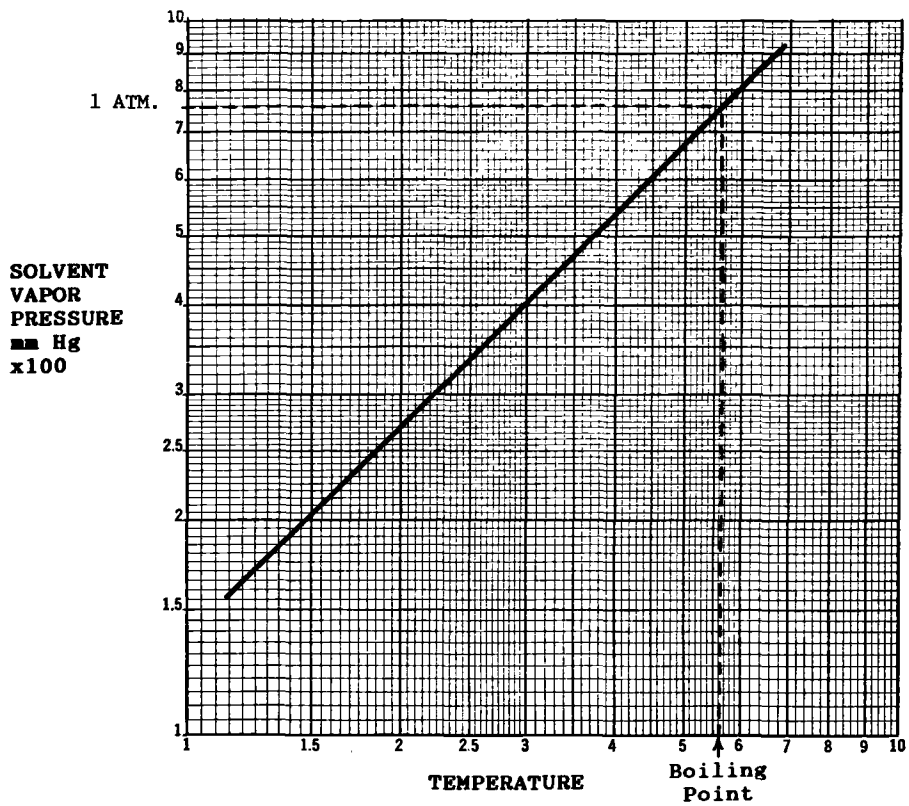

FIG. 9–Solvent vapor pressure versus temperature (idealized representation) [*30*].

ularly true for oxygenated solvents, which are relatively pure compounds. The more narrow the distillation range, the more pure is the solvent. Therefore, it is a useful test for detecting the presence of impurities or contaminants.

In addition, distillation temperature may be used to approximate the relative evaporation properties of one solvent versus another, although it does not provide precise information about evaporation rate. Evaporation/distillation temperature comparisons should not be made between dissimilar types of solvents since such predictions would be erroneous. However, for similar types of solvents, and for hydrocarbon solvents in particular, distillation data can be used effectively as a first approximation or gross measure of relative evaporation rate. For hydrocarbon solvents, the 50% distillation

point (i.e., the temperature at which 50% of the solvent has distilled) has been found to have a good correlation with evaporation rate [*8*].

The McArdle-Robertson evaporation index is based on the 50% distillation temperature [*31*]. It is intended primarily to apply to straight-run paraffinic naphthas having distillation ranges of not more than 40°C and to compare their relative evaporation times, as illustrated in Fig. 10.

There are three ASTM distillation test methods which are used for different kinds of solvents:

1. ASTM D 86, Distillation of Petroleum Products, is intended to be used for wide-boiling hydrocarbon solvents such as VM&P naphthas and mineral spirits.
2. ASTM D 850, Distillation of Industrial Aromatic Hydrocarbons and Related Materials, is intended for narrow-boiling aromatic solvents such as toluene, ethylbenzene, and xylenes.
3. ASTM D 1078, Distillation Range of Volatile Organic Liquids, is intended for narrow-boiling solvents, oxygenated solvents in particular, and also for certain hydrocarbon solvents, chlorinated solvents, and others.

The same solvent sample, tested by each of the three ASTM methods, may produce different distillation data due to variations in the equipment and procedures. It is important, therefore, when presenting distillation data or solvent specifications, to indicate the test method used.

The basic test procedure described in all three test methods is similar, although there are differences as noted in Table 12. The sample is heated in a glass distillation flask until it boils. Solvent vapors are cooled and condensed by passing them through a jacketed, water-cooled tube. Condensate is collected in a calibrated receiver. Distillation temperatures are registered on a thermometer immersed in the vapor in the neck of the distillation flask. Distillation temperatures are usually recorded at the initial boiling point, and when 5, 10, and each additional 10% up to 90%, and 95% of the sample have distilled over, and at the dry point. Typical distillation temperatures of selected commercial solvents are listed in Tables 1 through 9.

The basic assembly of the manual distillation apparatus is illustrated in Fig. 11. Automatic distillation equipment (Fig. 12) employing the same basic principles is available. The automatic equipment uses a thermocouple for temperature measurement and an automatic moving photocell sensing device to measure liquid level in the receiver. A recorder charts the volume of distillate recovered versus temperature.

There are specific terms to describe key temperatures in all ASTM distillations:

1. *Initial boiling point*—The temperature indicated by the distillation thermometer at the instant that the first drop of condensate falls from the condenser tube into the receiver.
2. *Dry point*—The temperature indicated at the instant that the last drop of liquid evaporates from the lowest point in the distillation flask.
3. *End point, final boiling point,* or *maximum temperature*—The maximum thermometer reading obtained during the test. This usually occurs after the evaporation of all liquid from the bottom of the distillation flask. If there are "heavies" in the sample, and there is no clean dry point, the end point is taken as the thermometer reading 5 min after the 95% distillation point.
4. *Decomposition Point*—The temperature reading that coincides with the first indication of decomposition of the liquid in the flask. Decomposition, if it occurs, is evidenced by smoke and fumes in the flask; the temperature ceases to rise and begins to fall.

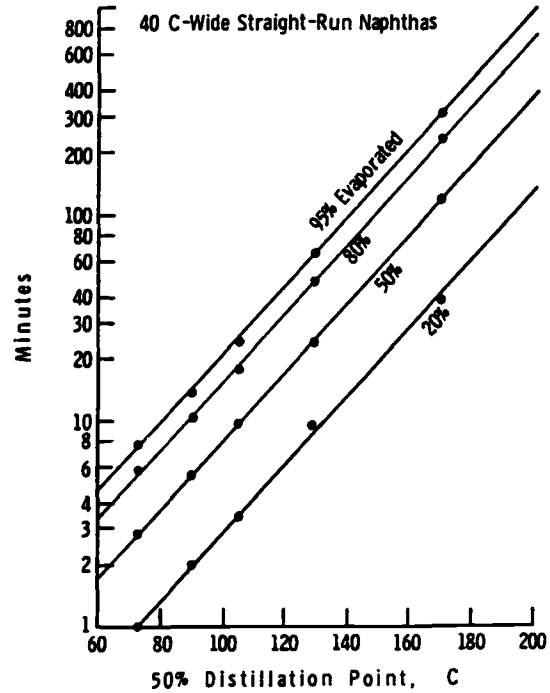

FIG. 10—McArdle-Robertson index for estimating evaporation rate from distillation temperatures (courtesy of *Industrial Chemistry*).

Two common sources of error or bias in distillation data are (a) improper placement of the thermometer in the distillation flask, and (b) failure to make appropriate corrections for barometric pressure. The thermometer must be positioned exactly as shown in Fig. 13. Higher placement will result in consistently lower temperature readings; lower placement may give higher readings.

Distillation temperature readings must be corrected for deviations from standard sea-level barometric pressure. Otherwise, tests run at high altitude or low barometric pressure will result in inaccurate, low distillation temperatures, while high barometric pressure will cause high distillation temperatures. Correction factors appropriate for specific solvents are listed in the ASTM test methods.

Flash Point

Flash point is another manifestation of volatility. The flash point of a liquid is defined as the lowest temperature at which the liquid gives off enough vapor to form an ignitable mixture with air to produce a flame when a source of ignition is brought close to the surface of the liquid under specified conditions of test at standard barometric pressure (760 mmHg, 101.3 kPa). Appropriate corrections must be made for barometric pressure deviations from standard pressure since flash point is dependent on vapor concentration, which is governed by vapor pressure.

TABLE 12—Comparison of ASTM distillation test methods for solvents.

Sample Type	ASTM D 86, Wide-Boiling Hydrocarbons	ASTM D 850, Narrow-Boiling Aromatics	ASTM D 1078, Narrow-Boiling Oxygenated (and others)
Sample size, mL	100	100	100
Distillation flask size, mL	125	200	200
Number of specified thermometers	2	8	14
Insulating shield hole size, mm	50	25–50[a]	38
Condenser temperature, °C	0–60[a]	10–20	0–50[a]
Rate of heat up to IBP, time, min	5–15[a]	5–10	5–15[a]
Rate of distillation, mL/min	4–5	5–7	4–5
95% point to EP, time, min	5	...	5

[a]Varies depending on boiling point and range of sample.

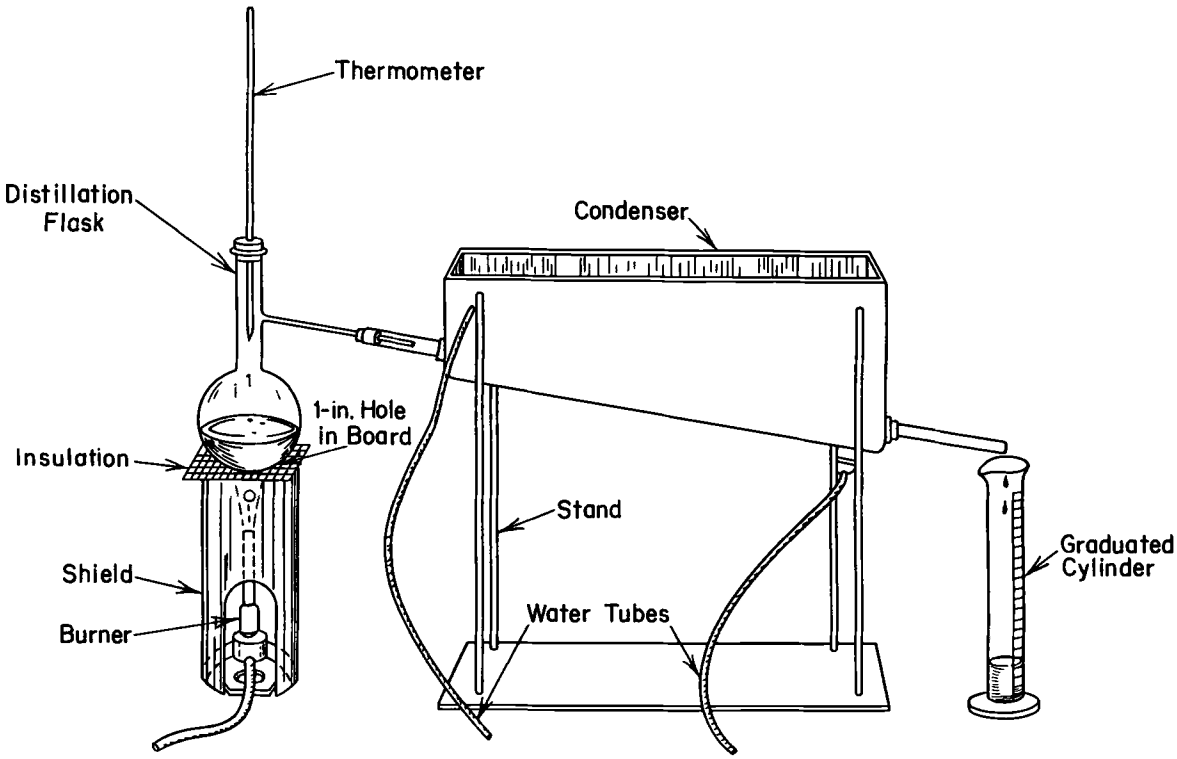

FIG. 11–Apparatus assembly for distillation test.

Similar to the vapor pressure/temperature relationship, solvent vapor pressure *concentration* in air is also a function of temperature, as shown in the generalized illustration in Fig. 14 [*30*]. At low temperatures, there is insufficient vapor concentration (fuel) available to ignite and produce a flame. In this temperature region below the flash point temperature, the solvent vapor cannot be ignited by a spark or flame.

As the temperature of the solvent is gradually increased, there is an accompanying increase in vapor concentration above the surface of the liquid. At a certain temperature, there will be sufficient vapor (fuel) to form a flammable (or explosive) mixture, and a fire will occur if a spark or flame is introduced. The temperature of the liquid at this point is called the "flash point," and the concentration of vapor at this temperature is called the "lower flammable limit" or "lower explosive limit" (LEL). Typical flash points of selected commercial solvents are listed in Tables 1 through 8.

At temperatures above the flash point, a flammable mixture of solvent vapor and air is present above the surface of the solvent. Just as "flash point" represents the lower temperature limit for ignition, there is also an upper limit beyond which the vapor/air mixture is too rich to ignite and burn. The vapor concentration at the upper temperature limit is called the "upper flammable limit" or "upper explosive limit" (UEL). *It must be emphasized that these phenomena apply only to equilibrium, closed systems.* For hydrocarbon solvents, the LEL is usually about 1 vol% solvent vapor in air, and the UEL is about 7 vol%, but for oxygenated solvents, these values can vary over a wide range.

Flash point is one indicator of the relative flammability hazard of solvents and solvent-containing products. The U.S. Department of Transportation (DOT) and the U.S. Department of Labor (OSHA) designate "flammable liquids" as those having flash points below 100°F (38°C). These require special packaging and handling. International cargo regulations specify a 140°F (60°C) flash point as the upper limit for "flammable liquids." In addition to being used to classify materials in government regulations, flash point limits are

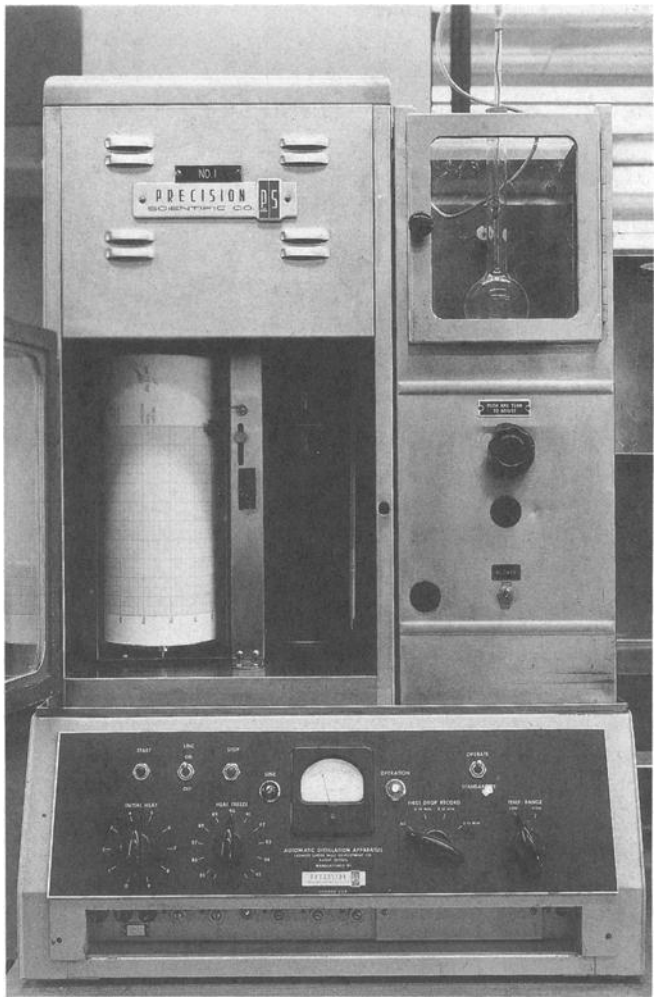

FIG. 12–Automatic distillation apparatus.

often listed as one of the requirements in solvent specifications, for hydrocarbon solvents in particular. Flash point may also be used to indicate the presence of impurities or contaminants in a given liquid, such as the presence of residual solvents in solvent-refined drying oils.

Flash point is roughly inversely proportional to volatility. The most volatile solvents tend to have the lowest flash points, which are indicative of the greatest fire hazard. With mixtures of miscible solvents, the component having the lowest flash point largely determines the flash point of the mixture when that component is present in substantial proportion, e.g., 5% or more. Mutually miscible mixtures of flammable/nonflammable liquids exhibit a direct, though often complex, relationship between flash point and the concentration of the flammable component, e.g., alcohols and water.

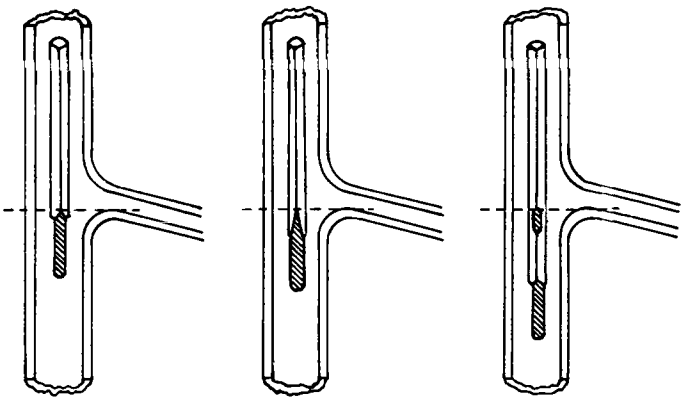

FIG. 13–Position of thermometer in distillation flask.

Chlorinated solvents, most of which are nonflammable, will have various effects in mixtures with flammable solvents. Some will suppress (i.e., raise or prevent) the flash point of flammable liquids because of the high vapor pressure of the nonflammable chlorinated solvent. However, some mixtures of chlorinated solvents and flammable liquids will lower the flash point below that of the flammable liquid, e.g., mineral spirits and methylene chloride [*32*].

It is good practice to actually measure the flash point of solvent blends because of the uncertainty of making predictions. There are several test methods commonly used.

Tag Open Cup—ASTM Method D 1310, Flash Point and Fire Points of Liquids by Tag Open-Cup Apparatus, may be used for determining the *open cup* flash points of liquids having flash points between zero and 325°F (−18 and 165°C). The sample is cooled to at least 20°F (11°C) below the expected flash point, and it is placed in an uncovered cup jacketed by a heat transfer fluid. The sample cup is filled to a depth of approximately ⅛ in. below the edge, and it is heated at a slow, constant rate. Temperature is measured by a thermometer immersed in the sample. A small test flame is passed at a uniform rate across the surface of the cup at 2°F (1°C) intervals of temperature rise until a flash of flame is observed. The sample temperature corresponding to the flash of flame is the "flash point" (Fig. 15).

"Fire point" can be determined with the same apparatus by continuing the test. Fire point is defined as the lowest temperature at which sustained burning of the sample takes place for at least 5 s.

Although the Tag Open Cup Flash Point test may appear to represent real life situations of open containers or accidental solvent spills, the test results could be misleading, especially for solvent blends. As the sample is slowly heated, the lightest, most volatile component in the blend may escape without being ignited. Therefore, *closed cup* test methods are now preferred by most regulatory agencies.

Tag Closed Cup—ASTM Method D 56, Flash Point by Tag Closed Cup Tester, uses an apparatus which confines solvent vapors in a closed cup (Fig. 16). It is intended for testing liquids (a) which contain no suspended solids, (b) which do not form a surface film under test conditions, (c) with viscosities below 9.5 cSt at 77°F (25°C) or below 5.5 cSt at 104°F (40°C), and (d) flash points below 200°F (93°C).

The 50-mL sample, cup, and heat transfer fluid in the cup jacket are cooled to 20°F (11°C) below the expected flash point. With the cup lid closed, the sample is heated at a specified slow, constant rate, as measured by a thermometer immersed in the sample. A small test flame of specified size is momentarily directed into the cup through an opening in the lid that is simultaneously opened at regular intervals of temperature rise; after each 1°F (0.5°C) for samples with flash points below 140°F (60°C) or 2°F (1°C) for samples with flash points above 140°F. The flash point is taken as the lowest temperature at which application of the test flame causes the vapor in the cup to ignite.

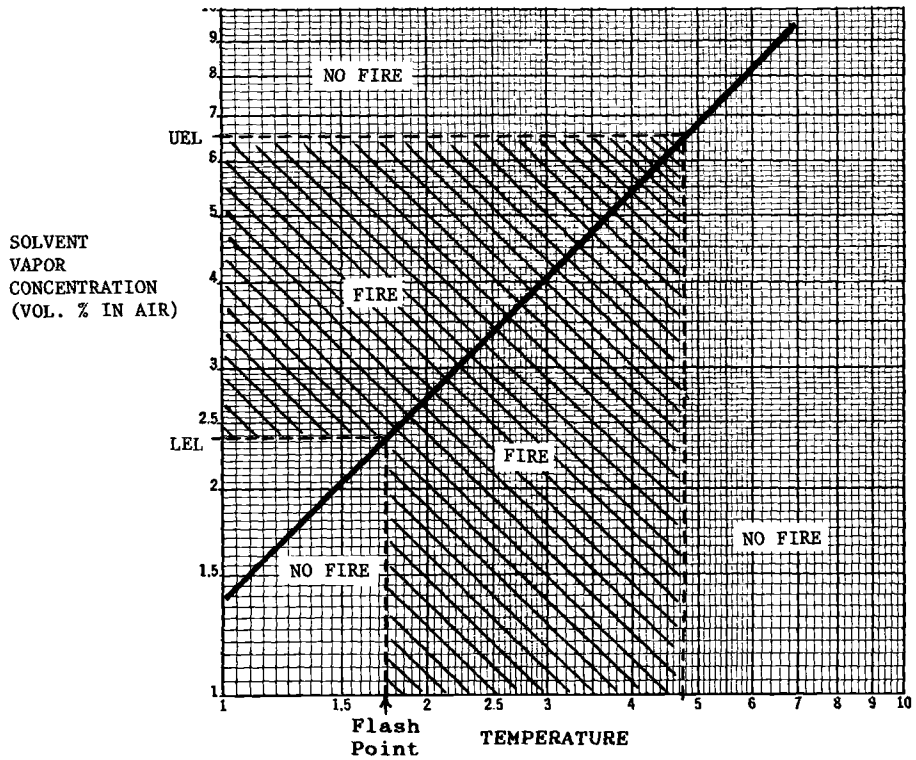

FIG. 14–Solvent vapor concentration versus temperature (idealized representation) [*30*].

Pensky-Martens—ASTM Method D 93, Flash Point by Pensky-Martens Closed-Cup Tester, is intended to be used for viscous liquids, suspensions of solids, and liquids that tend to form a surface film under test conditions. It differs from the Tag Closed Cup Test in that (a) it employs an air bath device instead of a liquid jacket around the test cup, and (b) the sample is mechanically stirred during the test (Figs. 17 and 18). This test method is particularly suited for samples such as resin solutions, paints, varnishes, lacquers, printing inks, and certain adhesives. Materials with flash points as high as 285°F (140°C) can be tested.

The sample and tester are first brought to a temperature of 60°F (15°C) or 20°F (11°C) lower than the expected flash point, whichever is lower. The sample is then heated at a slow, constant rate with continual stirring to provide uniform temperature throughout and to prevent formation of a surface film which would otherwise retard solvent vaporization. A small test flame is momentarily directed into the cup through a shuttered opening in the lid at regular temperature intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame causes vapor in the cup to ignite.

Setaflash—ASTM Method D 3278, Flash Point of Liquids by Setaflash-Closed-Cup Apparatus, describes procedures for (a) determining whether a material does or does not flash at a specified temperature, or (b) determining the lowest finite temperature at which a material does flash. The test methods are applicable to paints, enamels, lacquers, varnishes, and related products having a flash point between 32 and 230°F (0 and 110°C) and viscosity lower than 150 St at 77°F (25°C). These test methods are similar to international standards ISO 3679 and ISO 3680.

The Setaflash apparatus has certain advantages over other flash point measuring devices. It requires only a 2 to 4-mL sample instead of 50 to 70 mL. In the flash point verification mode of operation, test time is only 1 or 2 min (Fig. 19).

To perform a "flash/no flash" test, 2 mL of sample is introduced by means of a syringe through a leakproof entry port into the tightly closed Setaflash tester or, with very viscous materials, directly into the cup that has been brought to the required test temperature. As a "flash/no flash" test, the expected flash point temperature may be a specification or other operating requirement. After 1 min, a test flame is applied inside the cup and note is taken whether or not the specimen flashes. A fresh specimen must be used if a repeat test is necessary.

For a finite flash point measurement, the temperature is sequentially increased through the anticipated range, the test flame being applied at 9°F (5°C) intervals until a flash is observed. A true determination is then made using a fresh specimen, starting the test at the temperature of the last interval before the flash point of the material and making tests at increasing 1°F (0.5°C) intervals.

Equilibrium Flash Point—The Tag Closed Cup and Pensky-Martens flash point test methods depend on a definite rate of temperature increase to control the precision of the test method. However, the rate of heating may not in all cases give the accuracy expected because of the low thermal conductivity of some liquids such as paints, resin solutions, and related viscous materials. To reduce this effect, ASTM Method D 3941, Flash Point by the Equilibrium Method with a Closed-Cup Apparatus, uses a slow rate of heating to provide a uniform temperature throughout the specimen.

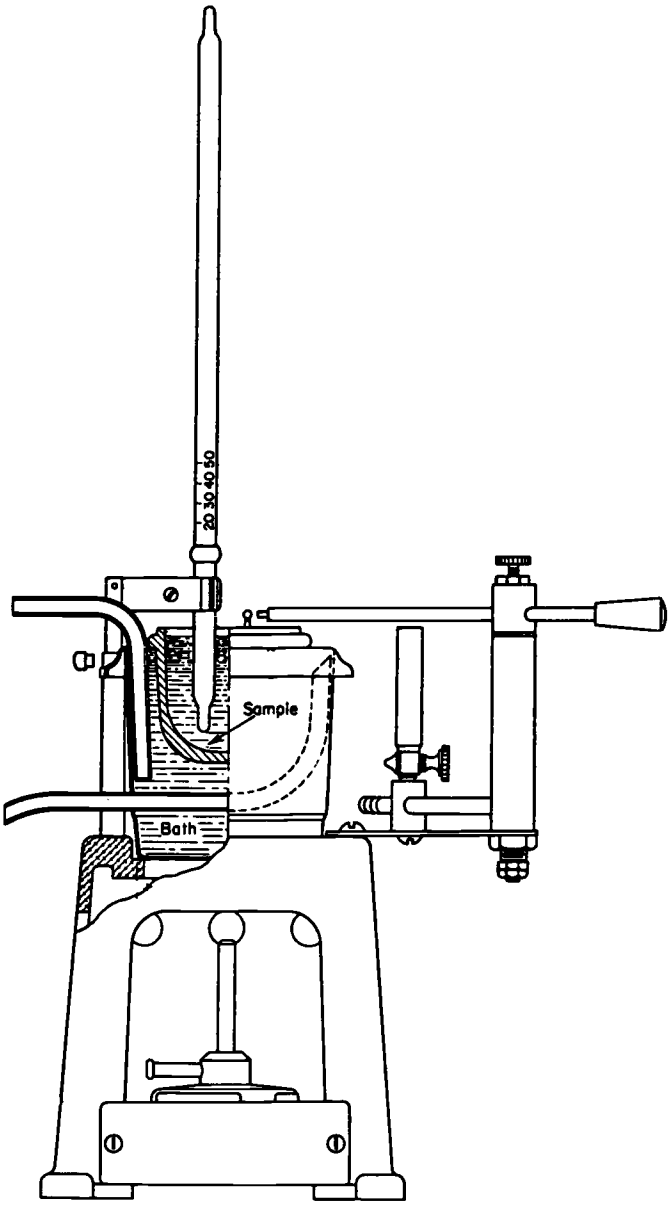

FIG. 15–Tag open-cup flash point tester.

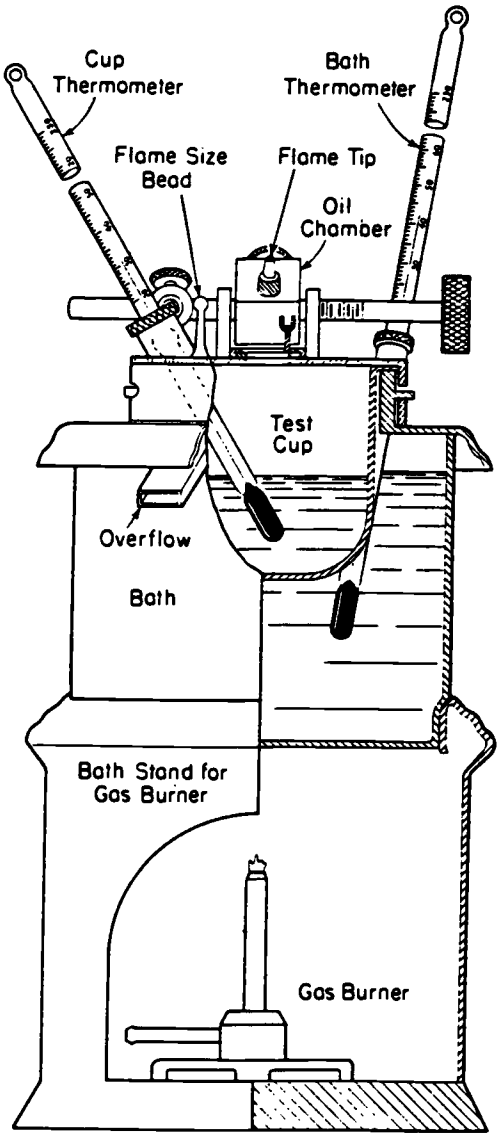

FIG. 16–Tag closed-cup flash point tester.

The specimen is heated in a closed cup of standard design in a suitable water bath at a rate of 1.0°F (0.5°C) in not less than 1.5 min so that the difference in temperature between the specimen in the cup and the bath never exceeds 3.5°F (2.0°C). Flash determinations are made at intervals of not less than 1.5 min. Since the specimen is heated at a reduced rate, a longer time interval between each determination is necessary to re-establish the saturation concentration of vapor in the air space above the specimen after each flash test.

Equilibrium Flash/No Flash—ASTM Method D 3934, Flash/No Flash Test—Equilibrium Method by Closed-Cup Apparatus, does not determine a finite flash point, but it verifies whether or not flashing occurs at a single specified temperature, which may be a product specification or agency requirement. The determination is made more accurate by ensuring that the flash test is carried out only when the material under test and the air/vapor mixture above it are in approximate equilibrium at the specified temperature.

Standard closed cups are used, i.e., Tag, Pensky-Martens, or Setaflash, and this test is run such that the air/vapor space above the specimen attains a saturation concentration of vapor before the test flame is applied. The specimen is held at the specified temperature for at least a 10-min period before the test flame is applied. This test method does not provide for the determination of the actual flash point, but only whether a specimen does or does not flash at a specified temperature.

PHYSICAL PROPERTIES

Density and Specific Gravity

Significance

Specific gravity is an inherent property which is listed as a requirement in all solvent specifications and is often used to set specifications. It is a good, simple, qualitative test when used with other tests to establish or confirm the identity of a solvent. In addition, it is useful for quality control, to provide

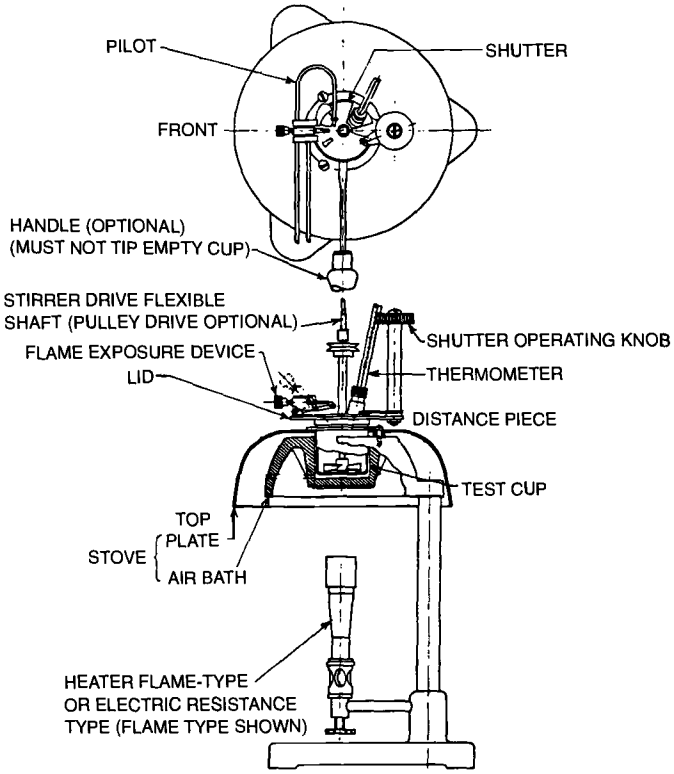

FIG. 17–Pensky-Martens closed-cup flash point tester.

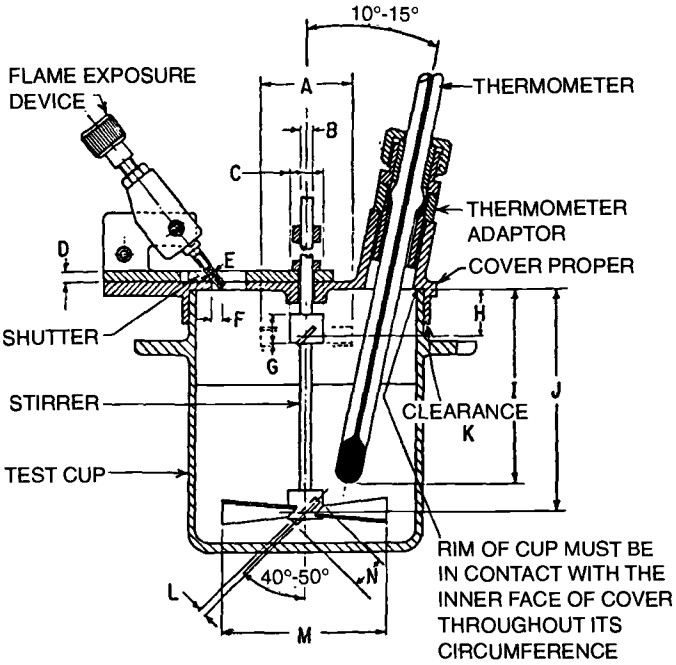

FIG. 18–Pensky-Martens flash point test cup and cover assembly.

a check on product uniformity, and to detect gross contamination.

Accurate specific gravity values are essential for the calculation of the volume occupied by a product whose weight is known or of the weight of a product when the volume is known. This information is necessary for accurately surveying large shipments by vessels, barges, railroad tank cars, or tank trucks to calculate costs and freight rates, and for inventory measurement and control.

It is customary to buy and sell hydrocarbon solvents on a volumetric basis (e.g., gallons, litres), converting measured values to volume at a standard temperature of 60°F (15.56°C). International transactions, however, are made on a gravimetric basis (e.g., metric tons) calculated at a standard 60°F temperature.

For oxygenated and other solvents, commercial transactions are customarily made on a gravimetric basis (e.g., pounds, kilograms, tons) converting measured values to weight at a standard temperature of 20°C (68°F). However, there is a trend toward changing the standard temperature to 25°C (77°F).

Finally, a knowledge of specific gravities of solvents and other paint components is important for the formulation of paints, varnishes, and lacquers. It is often necessary to make conversions between weight and volume bases and to calculate parameters such as pounds per gallon or kilograms per litre.

Typical specific gravities of selected commercial solvents are listed in Tables 1 through 9.

Definitions

The terminology relating to density and specific gravity is often confusing: density and apparent density, specific gravity and apparent specific gravity, mass and apparent mass versus weight. Definitions for these terms as they are applied in ASTM standards are contained in ASTM E 12, Definitions of Terms Relating to Density and Specific Gravity of Solids, Liquids, and Gases. Key definitions pertaining to liquid solvents are as follows.

density—the mass of a unit volume of a material at a specified temperature. The units shall be stated, such as grams per millilitre, grams per cubic centimetre, pounds per cubic foot, or other. The form of expression shall be

"density at x"

where x is the temperature of the material.

density, apparent—the weight in air of a unit volume of a material at a specified temperature. The units shall be stated. The form of expression shall be

"apparent density at x"

where x is the temperature of the material.

specific gravity—the ratio of the mass of a unit volume of a material at a stated temperature to the mass of the same volume of gas-free distilled water at a stated temperature. The form of the expression shall be

"specific gravity x/y°C"

where x is the temperature of the material and y is the temperature of the water. The term "relative density" with the same meaning as specific gravity is becoming more widely used than "specific gravity."

specific gravity, apparent—the ratio of the weight in air of a unit volume of a material at a stated temperature to the weight in air of equal density of an equal volume of gas-free distilled water at a stated temperature. The form of expression shall be

"apparent specific gravity x/y°C"

where x is the temperature of the material and y is the temperature of the water.

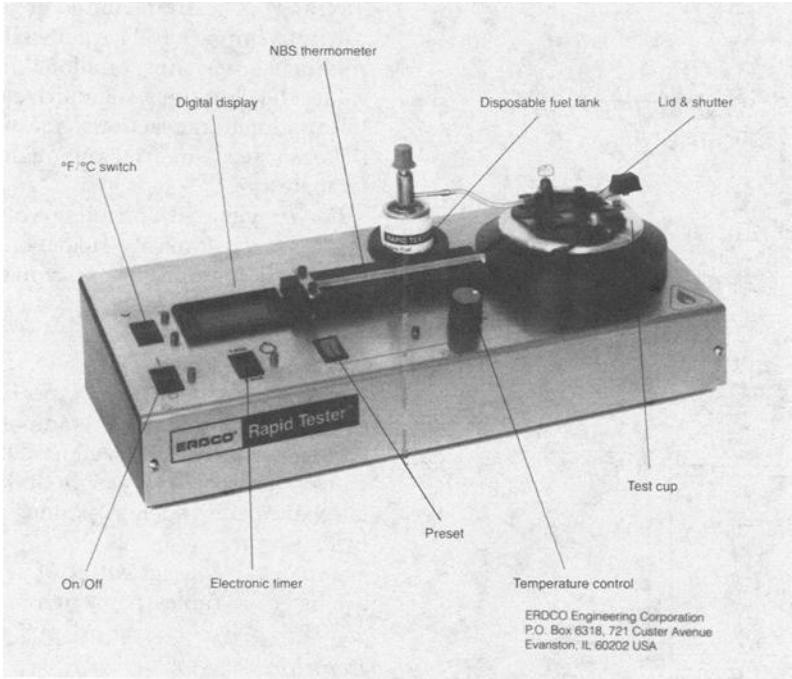

FIG. 19–Setaflash tester.

API gravity—a special function of relative density (specific gravity) 60/60°F (15.56/15.56°C) represented by:

$$\text{API gravity, degrees} = \frac{141.5}{\text{sp gr } 60/60°\text{F}} - 131.5$$

No statement of reference temperature is required, since 60°F is included in the definition. API gravity applies specifically to crude petroleum and to petroleum products such as hydrocarbon solvents. Gravities are determined at 60°F (15.56°C) or are converted to values at 60°F by means of standard tables. These tables are *not applicable* to nonhydrocarbons nor to essentially pure hydrocarbons such as the aromatics.

A brief discussion of these definitions may be useful. In scientific terminology, *mass* is a measure of the quantity of material in a body, and it is constant regardless of geographical location, altitude, or atmospheric conditions as long as no material is added or taken away. *Weight* is the force with which a body is attracted to the earth, and it varies from place to place with the acceleration of gravity.

When an equal-arm balance is used to compare an object with standards of mass ("weights"), the effects of variations in the acceleration of gravity are self-eliminating and need not be taken into account, but the apparent mass of the object is slightly different from the true mass because of the buoyant effects of the surrounding air. Mass can then be computed from apparent mass by applying a correction for air buoyancy. When a spring balance is used, an additional correction accounting for the local value of the acceleration of gravity is required for the computation of mass.

For many commercial and industrial processes the scientific distinction between mass, apparent mass, and weight is of no practical consequence and is therefore ignored. The term "weight" in general practice has been accepted as being the value secured when an object is weighed in air. This "weight" or "weight in air" is often converted to "weight in vacuo" by the application of an air buoyancy correction, and it is then considered synonymous with mass.

All of the definitions listed above are based on either "mass" or "weight in air," with the distinction being that air buoyancy corrections have been applied in the former case and not in the latter. Density and specific gravity are based on mass and should be similarly constant. Apparent density and apparent specific gravity are based on weight in air, and therefore they are subject to change with atmospheric conditions, locality, and altitude. These changes may be negligible, depending on the accuracy required for the particular application.

Hydrometer Methods

Hydrometer methods are the quickest, simplest means for measuring density, specific gravity (relative density), and API gravity, especially in the field. These methods are based on the principle that the specific gravity of a liquid varies directly with the depth of immersion of a body floating in it. The floating body, called a hydrometer, is graduated in units of density, specific gravity, or API gravity units. Hydrometers are useful when accuracy to three decimal places is adequate.

The sample is brought to the prescribed temperature, and it is transferred to a clear glass or plastic cylinder which is at approximately the same temperature. The appropriate hydrometer, having the scale of interest, is lowered into the sample and is allowed to float freely and settle. After temperature equilibrium has been reached, the hydrometer scale is read. Note is made of the hydrometer scale graduation nearest to the apparent intersection of the horizontal plane surface of the liquid (Fig. 20). Temperature of the sample is read from a separate thermometer or from a thermometer integrated into the design of the hydrometer.

Detailed descriptions of test methods for the proper use of hydrometers can be found in ASTM Method D 891 (Method

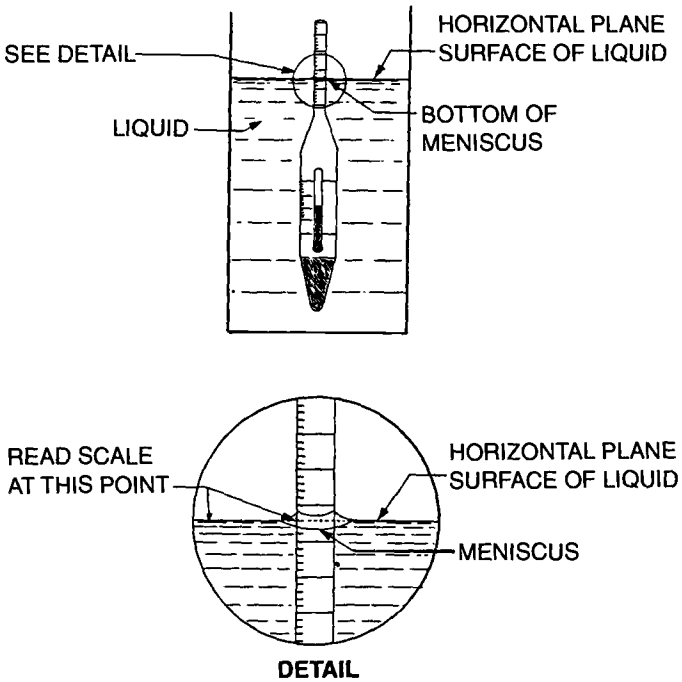

FIG. 20–Hydrometer and Meniscus detail.

A), Specific Gravity, Apparent, of Liquid Industrial Chemicals; ASTM Method D 287, API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method); and ASTM Method D 1298, Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method.

For hydrocarbon solvent naphthas, values can be measured on a hydrometer at convenient temperatures, the readings of density may then be reduced to 15°C, and readings of relative density (specific gravity) and API gravity at 60°F are obtained by means of international standard tables. By means of these tables, values determined in any one of the three systems of measurement are convertible to equivalent values in either of the other two systems so that measurements may be made in the units of local convenience.

Pycnometer Methods

Pycnometer methods for measuring specific gravity are more accurate and precise than hydrometer methods. They are used when accuracy to four or more decimal places is required. ASTM Method D 891 (Method B), Specific Gravity, Apparent, of Liquid Industrial Chemicals, describes the general test method for using a pycnometer.

A pycnometer is a tared vessel which is filled with water and weighed. It is then filled with the sample and weighed. Water, sample, and pycnometer are at a specified temperature. The ratio of the weight of sample to weight of water in air is the apparent specific gravity.

Bingham Pycnometer—A Bingham-type pycnometer may be used when density or specific gravity needs to be determined to five decimal places (Fig. 21). Its use is described in ASTM Method D 1217, Density and Relative Density (Specific Gravity) of Liquids by Bingham Pycnometer.

The pycnometer is first carefully calibrated by determining the weight of freshly boiled and cooled distilled water (distilled from alkaline permanganate through a tin condenser)

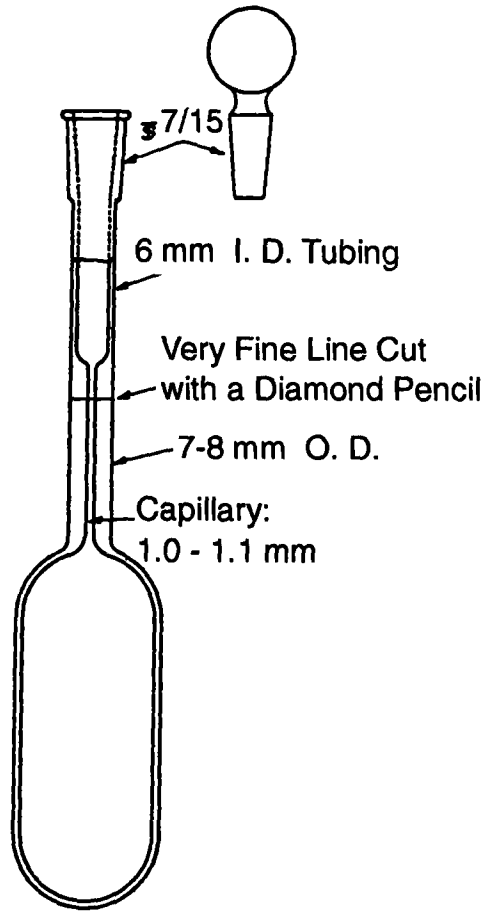

FIG. 21–Bingham-type pycnometer.

held by the pycnometer when equilibrated to volume at the bath temperature to be used for the determination. The liquid sample is introduced into the tared, clean, dry pycnometer, equilibrated to the desired temperature, and weighed. The relative density (specific gravity) or density is then calculated from this weight and the previously determined weight of water required to fill the pycnometer at the same temperature, both weights being corrected for the buoyancy of air.

Lipkin Bicapillary Pycnometer—The Lipkin bicapillary pycnometer is another type that is capable of high accuracy and precision when density or specific gravity needs to be determined to five decimal places [*33*]. Its use is described in ASTM Method D 941, Density and Relative Density (Specific Gravity) of Liquids by Lipkin Bicapillary Pycnometer.

The liquid sample is drawn into the pycnometer and weighed. It is then equilibrated at the test temperature, and the positions of the liquid levels in the capillaries are observed (Fig. 22). The density or relative density of the sample is then calculated from its weight, a calibration factor proportional to an equal volume of water, and a term that corrects for the buoyancy of air.

Digital Density Meter

A rapid, direct-reading, instrumental method for measuring density or specific gravity is by means of a digital density meter. Its use is described in ASTM Method D 4052, Density and Relative Density of Liquids by Digital Density Meter. A small amount of sample (several millilitres) is introduced

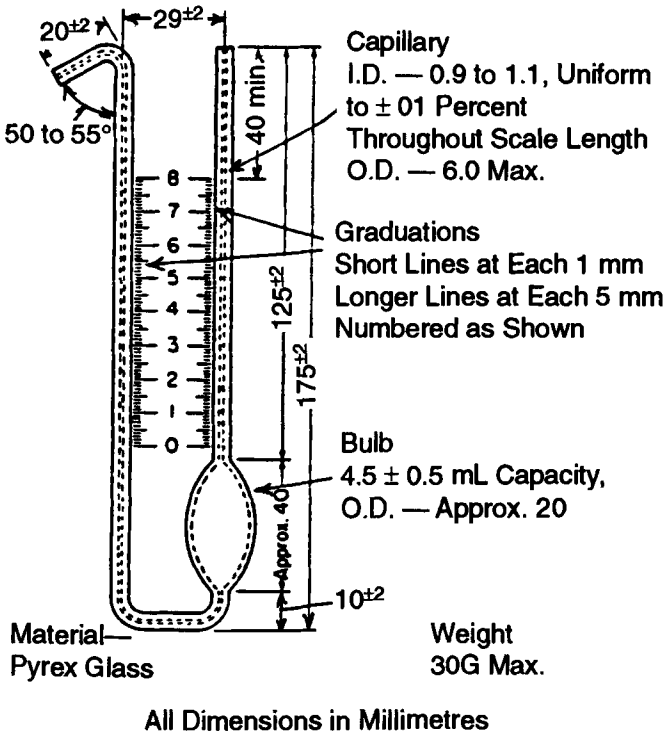

FIG. 22–Lipkin-type pycnometer.

into a vibrating quartz tube in the instrument at a preset temperature. Operation of the instrument is based on the principle that the oscillation of the quartz tube is damped as a function of the density of the sample within it. The instrument provides a digital readout of either density or specific gravity.

Calculations and Conversion Tables

ASTM Standard D 1250, Petroleum Measurement Tables, is a description of the tables which comprise Chapter 11, Section 1, of the *API Manual of Petroleum Measurement Standards* and which are distributed in three base systems of measurement: °API, °F, 60°F; relative density, °F, 60°F; and kilograms per cubic meter, °C, 15°C. These tables apply to crude petroleum and to all normally liquid petroleum products derived therefrom, which includes hydrocarbon solvent naphthas. They do *not* apply to oxygenated and other solvents nor to pure hydrocarbon solvents such as the aromatics.

ASTM Method D 1555, Calculation of Volume and Weight of Industrial Aromatic Hydrocarbons, contains tables for use in calculating the weights and volumes of the following solvents: benzene, toluene, mixed xylenes, *o-,m-,p*-xylene, cumene, ethylbenzene, high-flash aromatic naphthas, and cyclohexane. A method is given for calculating the volume at 60°F from an observed volume at any convenient temperature.

ASTM Method D 3505, Density or Relative Density of Pure Liquid Chemicals, describes the measurement of density or relative density using a Lipkin bicapillary pycnometer, and it provides methods for reporting results in the following units.

Density, g/cm^3 at 20°C
Density, g/mL at 20°C
Relative density, 20°C/4°C
Relative density, 60°F/60°F (15.56°C/15.56°C)
Commercial density, pounds (in air)/U.S. gal. at 60°F
Commercial density, pounds (in air)/U.K. gal. at 60°F

Tables of factors versus temperature are presented for benzene, toluene, mixed xylenes, *o-,m-,p*-xylene, and cyclohexane.

ASTM Method D 2935, Apparent Density of Industrial Aromatic Hydrocarbons, describes the measurement of apparent density in pounds (in air) per U.S. gallon at convenient temperature using a hydrometer and reporting values at any specified temperature. This method contains tables of "pounds in air per U.S. gallon" versus temperature. It applies only to the following solvents: benzene, toluene, mixed xylenes, *o-,m-,p*-xylenes, ethylbenzene, and cyclohexane.

ASTM Method E 201, Calculation of Volume and Weight of Industrial Chemical Liquids, presents tables for use in calculating the volume and weight of the following solvents: acetone, ethyl acetate (85 to 88 wt%), ethylene dichloride, ethylene glycol monomethyl ether, isobutyl alcohol, isopropyl alcohol (anhydrous), isopropyl alcohol (91 vol%), methyl ethyl ketone, methyl isobutyl ketone, and perchloroethylene.

A method is given for calculating the volume at 60°F from a volume observed at another convenient temperature. (Tables at 20°C can be calculated from the data and information provided.)

Also, a method is given for determining the weight in pounds per U.S. gallon (in air) at 60°F from an observed specific gravity and to compute therefrom the weight in pounds of a given volume of the liquid in U.S. gallons at 60°F.

Color

Most solvents are "water-white" or clear and essentially colorless. Color is an important specification requirement. If a solvent has color greater than the specification limit, it may be an indication of (a) inadequate processing, (b) contamination that might have occurred during storage and distribution, e.g., pickup of rust from tanks or pipes or color extracted from improper tank linings or loading hoses, or (c) oxidative degradation as a result of aging.

The property of color of a solvent varies in importance with the application for which the solvent is intended, the amount of color that can be tolerated being dependent on the color characteristics of the material in which it is used. For example, solvent color may undesirably contribute color to white paints or to fabrics if it is used for dry cleaning. Solvents that are off-specification in color are often found to be off-specification in other properties as well.

There are two visual test methods used for measuring the color of solvents; Platinum-Cobalt Color and Saybolt Color. Table 13 compares the approximate color values of the two scales.

Platinum-Cobalt Color

ASTM Method D 1209, Color of Clear Liquids (Platinum-Cobalt Scale), describes a procedure for the visual measurement of the color of nearly colorless liquids. It is used for all oxygenated solvents, most other solvents, and is gradually

TABLE 13—Approximate comparison of platinum-cobalt and Saybolt color scales.

	Platinum-Cobalt Color, ASTM D 1209	Saybolt Color, ASTM D 156
Lightest	0	+30
	10	+28
	20	+26
	30	+23
	40	+21
	50	+19
	70	+15
	100	+10
	150	+3
	180	0
	200	−3
	250	−8
Dark amber	300	−23

being used also for hydrocarbon solvents, where Saybolt Color still predominates.

For a number of years the term "water-white" was considered sufficient as a measurement of solvent color. Several expressions for defining "water-white" gradually appeared, and it became evident that a more precise color standard was needed. This was accomplished in 1952 with the adoption of ASTM Test Method D 1209 using the platinum-cobalt (Pt-Co) scale.

This test method is similar to the description given in "Standard Methods for the Examination of Water and Waste Water" [*34*] and is sometimes referred to as "APHA Color." The properties of these platinum-cobalt color standards were originally described by A. Hazen in 1892 in a paper entitled, "New Color Standard for Natural Waters" [*35*]. He assigned the number 5 (parts per ten thousand) to his platinum-cobalt stock solution.

Subsequently the American Public Health Association (APHA) in their first edition (1905) of "Standard Methods for the Examination of Water" used exactly the same concentration of reagents as did Hazen, and they assigned the color designation 500 (parts per million) to the same stock solution. (The parts per million nomenclature is not used since color is not referred directly to a weight relationship.)

The terms "Hazen Color" and "APHA Color" should not be used for solvents because they refer primarily to water. The recommended nomenclature for referring to the color of organic liquids is "Platinum-Cobalt Color, Test Method D 1209."

The method involves comparing visually the color of the solvent sample with colors of standard dilutions of the Pt-Co stock reference solution in Nessler tubes. The tubes are viewed vertically. The color standards are aqueous solutions of mixtures of cobalt chloride, potassium chloroplatinate, and hydrochloric acid. The scale runs from zero for pure water to 500 for the stock solution of 1.000 g of cobalt chloride, 1.245 g of potassium chloroplatinate, and 100 mL of hydrochloric acid made up to 1 L of solution. Most solvents have color values of less than 5 on the Pt-Co scale.

Saybolt Color

ASTM Method D 156, Saybolt Color of Petroleum Products, is used most often to measure the color of hydrocarbon solvents. This system of color measurement is not commonly employed outside of the petroleum industry.

In this method, a column of sample is viewed vertically, and its color is compared with that of a reference glass disk in the Saybolt chromometer. The height of the column of liquid is adjusted until the observed color intensity is equal to that of the colored glass disk. The depth of the liquid column is a measure of the Saybolt color, which is read directly from a scale on the instrument. The scale runs from +30 for colorless liquids to −30 for dark liquids.

Odor

Odor is an inherent, characteristic property of most solvents. Evaluation of the *characteristic odor* by a trained person is a quick and simple means of identifying a solvent (when combined with other tests) as well as for determining its suitability for an application from an odor point of view. *Residual odor* can be used to detect the presence of low-volatility materials that may be associated with manufacture, product degradation, or contamination during distribution.

ASTM Method D 1296, Odor of Volatile Solvents and Diluents, describes procedures for testing both the characteristic and residual odors of solvents. It involves dipping strips of filter paper into the sample and into a reference standard. To judge characteristic odor, an immediate comparison is made between the odor of the sample and reference standard on the filter paper. Residual odor is judged by permitting the papers to dry in air at room temperature and examining them at suitable time intervals for differences in odor.

Electrical Resistivity

Control of electrical resistivity is critical to the application of electrostatically sprayed coatings. It impacts the transfer efficiency (efficiency of paint application), coating appearance, and economics. Electrical resistivity of the paint must be properly adjusted to obtain optimum atomization characteristics and deposition. The adjustment is mainly accomplished through appropriate selection of solvents [*36*]. Nonpolar solvents, such as hydrocarbon solvents, have high electrical resistivity (low conductivity). Polar solvents such as ketones, alcohols, glycol ethers, and esters generally have low electrical resistivity (high conductivity), although some (e.g., higher molecular weight esters) have high resistivity. Typical values for commercial solvents are shown in Table 14.

An ASTM method, Electrical Resistivity of Liquid Paint and Related Materials is currently under development. It describes the use of two different test meters and probes, Ransburg and BYK-Gardner. Electrical resistivity values are often expressed in terms of "Ransburg megohms," which are read from the meter scale. Multiplication of these values by an appropriate cell constant, which is typically about 132, converts Ransburg megohms to specific resistivity in megohm-cm units.

Refractive Index

Refractive index is defined as the ratio of the speed of light through a vacuum to the speed of light through the sample. Although this property may have no fundamental signifi-

TABLE 14—Electrical resistance of typical commercial solvents.

	Ransburg Megohms
Hydrocarbon solvents	>20
Ketones	<1
Alcohols	<1
Glycol ethers	<1
Esters	
Ethyl acetate	6
n-butyl acetate	16
Hexyl acetate	>20
Ethoxyethyl acetate	3
Methoxypropyl acetate	3

cance to the practical solvent user and is generally not a specification requirement, the test is useful because measurements can be made quickly and precisely. As with specific gravity, refractive index is characteristic (although not uniquely so) of different solvents, and it is very sensitive to differences in composition of solvent blends. Therefore, it is useful for distinguishing between aromatic and saturated hydrocarbon solvents and for checking purity and uniformity of batches.

ASTM Method D 1218, Refractive Index and Refractive Dispersion of Hydrocarbon Liquids, is designed to measure these properties with high precision. For routine examination or quality control, simpler instruments with less accuracy are satisfactory.

PURITY AND COMPOSITION

Gas Chromatography

Gas chromatography (GC), also referred to as gas-liquid chromatography (GLC), is commonly used for the analysis of purity and composition of solvents. GC is a powerful analytical tool, very sensitive, rapid and simple in execution. It is capable of furnishing accurate qualitative and quantitative information from extremely small amounts of sample [*37*].

In this analytical technique, a minute amount of solvent sample (microlitres) is injected by means of a hypodermic syringe into a heated injection port in the instrument, where it is instantly vaporized. The solvent vapors are carried into a GC column by means of an inert carrier gas: helium, hydrogen, or nitrogen. The carrier gas is the eluent which transports the solvent components in vapor form through the GC column, which is maintained at a certain constant or programmed temperature.

The GC column consists of a long, coiled tube, typically ⅛- to ¼-in. inside diameter and made of stainless steel, copper, or glass. The tube is packed with a powdered, porous substrate or support, which is coated with an absorbent, stationary liquid phase. Alternatively, and in more common use today, the GC column consists of a long, coiled capillary tube 1/16-in. or less in diameter, which does not contain the powdered packing support. Instead, the interior walls of the capillary tube are coated with the liquid stationary phase.

The stationary liquid phase has the ability to preferentially adsorb certain components of the vaporized solvent sample. It is selected on the basis of the analysis to be performed. The stationary phase can in some cases be a nonpolar liquid, for instance a hydrocarbon oil, but in other cases a better separation of solvent components can be obtained by employing a highly polar liquid.

Actual separation of solvent components is achieved by a continuously alternating process of adsorption and vaporization as the solvent vapors pass through the GC column. Differences in adsorption characteristics and volatilities cause the individual sample components to pass through the column at different rates. The components are eluted from the column as individual bands separated by zones of inert carrier gas.

At the end of the GC column, the carrier gas and sample components flow through a sensitive detector, which is capable of indicating the presence of the components qualitatively and quantitatively. The detector may be a thermal conductivity cell, a flame ionization detector, or an electron capture detector. There are also other less common types of detectors.

TABLE 15—ASTM gas chromatography methods for analyzing purity and composition of solvents.

Compound	Method	Compound	Method
Benzene	D 4492	Mineral spirits (aromatics content)	D 3257
n-butyl acetate	D 3545	*i*-octane	D 2268
i-butyl acetate	D 3545	*n*-propyl acetate	D 3545
Cyclohexane	D 3054	*i*-propyl acetate	D 3545
Dipropylene glycol monomethyl ether	D 4773	*i*-propyl benzene	D 3760
Ethanol (SD-3A)	E 1100	Propylene glycol	E 202
2-ethoxyethyl acetate	D 3545	Propylene glycol monomethyl ether	D 4773
Ethyl acetate	D 3545	Propylene glycol monomethyl ether acetate	D 4773
Ethylene glycol	E 202	1,1,1-trichloroethane	D 3742
n-heptane	D 2268	Trichlorotrifluoroethane	D 3447
Methanol	E 346	Turpentine	D 3009
Methyl amyl ketone	D 3893	Xylenes (mixed)	D 2306
Methyl ethyl ketone	D 2804	*o*-xylene	D 3797
Methyl isoamyl ketone	D 3893	*p*-xylene	D 3798
Methyl isobutyl ketone	D 3329		

Any material other than the carrier gas going through the detector will cause a peak to be plotted on a recorder chart.

The time required for a component to flow through the column, under a given set of operating conditions, when compared to the time for known compounds, helps to identify the component. The amount of that component is proportional to the area under the recorder chart peak. Modern gas chromatographs often have a digital integrator which prints out the elution time and the area under the peak. Temperature, column length and size, type and amount of stationary liquid phase, carrier gas pressure and flow rate, and sample size are some of the variables that can be changed to effect desired separations.

Versatility of gas chromatography in solvent analysis is very great. Good ASTM references on gas chromatography include "ASTM Standards on Chromatography," second edition; ASTM Practice E 260, packed Column Gas Chromatography; and ASTM Practice E 355, Gas Chromatography Terms and Relationships. Specific ASTM GC methods for analyzing the purity and composition of solvents are listed in Table 15.

Liquid Chromatography

There are two ASTM methods which utilize a liquid chromatography procedure for measuring the volume percentages of aromatics, olefins, and saturated aliphatics (paraffins and naphthenes) which comprise a hydrocarbon solvent naphtha. Both methods involve the physical separation of these hydrocarbon types by passing the hydrocarbon sample through a tube packed with silica gel. The technique is based on the principle that polar compounds are adsorbed more strongly by silica gel than are nonpolar saturated compounds.

A hydrocarbon solvent sample is passed through a glass column packed with silica gel. Then, alcohol, which is more strongly adsorbed than any hydrocarbon, follows the sample through the column, desorbing and forcing the hydrocarbons out. Saturated compounds are eluted first, unsaturated compounds next, and then aromatics.

In ASTM Method D 936, Aromatic Hydrocarbons in Olefin-Free Gasolines by Silica Gel Adsorption, small samples of the emerging sample are periodically collected. The refractive index of each fraction is measured. From this information, the relative percentages of aliphatics and aromatics can be determined, as illustrated in Fig. 23. Precision is good, but the procedure is slow.

ASTM Method D 1319, Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption (FIA), is a refinement of the silica gel adsorption procedure. A mixture of fluorescent dyes is added to the hydrocarbon solvent sample before it is put into the silica gel column. When all of the sample has been adsorbed on the silica gel, alcohol is added under pressure to desorb and force the sample down the column. The fluorescent dyes are also selectively separated with the sample fractions, and they make the boundaries of the aromatics, olefins, and saturates clearly visible under ultraviolet light. The zone of aromatics fluoresces violet, and the zone of olefins fluoresces a chartreuse color. The zone of paraffins plus naphthenes remains colorless. Volume percentage of each hydrocarbon type is determined by measuring the length of each zone in a long, narrow extension of the silica gel column.

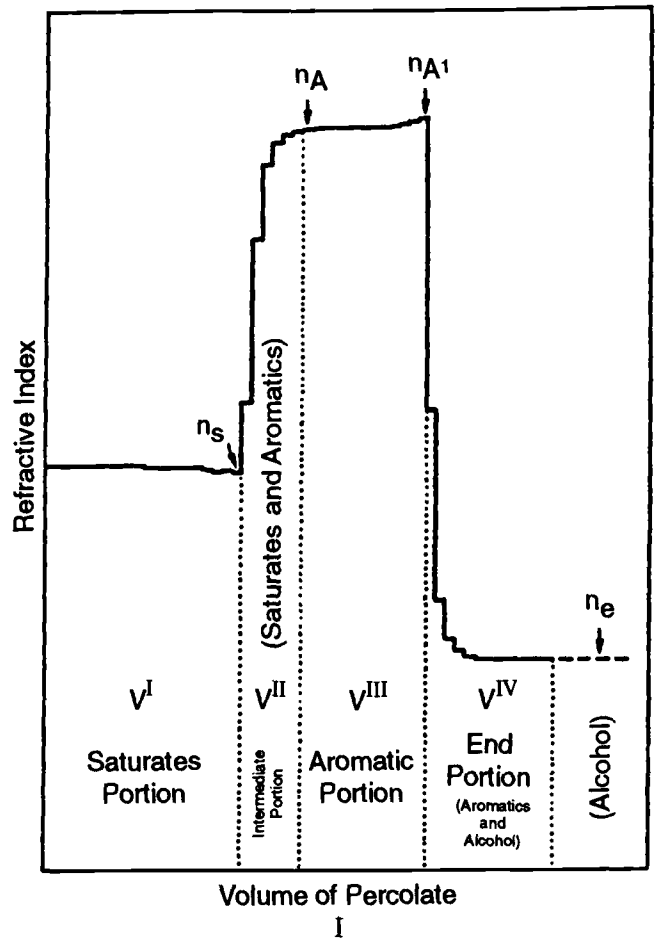

FIG. 23–Typical adsorptogram by ASTM Method D 936.

Purity of Ketones

ASTM Method D 2192, Purity of Aldehydes and Ketones, is an alternative to gas chromatography for measurement of the purity of ketone solvents. This is a wet chemical procedure and is applicable for testing ketones having greater than 98% purity.

The test is based on the reaction of ketones with hydroxylamine to form an oxime. Hydroxylamine hydrochloride is first converted in part to free hydroxylamine by reaction with a known amount of aqueous triethanolamine.

$$H_2NOH{\cdot}HCl + (HOCH_2CH_2)_3N \longrightarrow H_2NOH + (HOCH_2CH_2)_3N{\cdot}HCl$$

The free hydroxylamine then reacts with the ketone to form an oxime.

$$R_1R_2C = 0 + H_2NOH \longrightarrow R_1R_2C = NOH + H_2O$$

where R_1 and R_2 are alkyl groups.

The amount of hydroxylamine consumed, which is determined by titration of the excess base with standard sulfuric acid, using bromophenol blue indicator, is a measure of the ketone originally present. Water, alcohols, saturated esters,

and hydrocarbons do not react with the reagent, but large amounts of inert organic solvents are undesirable because of the possible effect on the indicator.

Purity of Esters

ASTM Method D 1617, Ester Value of Solvents and Thinners, is an alternative to gas chromatography for the measurement of purity of ester solvents. It may also be used for determining the ester content of lacquer thinners.

This is a wet chemical test and involves the reaction of the solvent sample with a measured excess of aqueous potassium hydroxide, using isopropanol as a mutual solvent if necessary

$$R_1COOR_2 + KOH \longrightarrow [R_1COO]^-K^+ + R_2OH$$

where R_1 and R_2 are alkyl groups. The amount of potassium hydroxide consumed, which is determined by titrating the excess with standard mineral acid, is a measure of the amount of ester originally present.

This test method has its greatest application where the solvent or thinner is not a pure ester. The type of ester present must be known to perform the calculations. The test may also be used for assessing compliance with ester specifications.

IMPURITIES

Acidity

Solvents may have residual acidity from manufacturing processes, or acidity may be present as a result of contamination or decomposition during storage or distribution. Acidity is undesirable since it may cause corrosion of storage tanks and lines. Also, it may cause reactions with basic pigments resulting in color changes.

ASTM Method D 847, Acidity of Benzene, Toluene, Xylenes, Solvent Naphthas, and Similar Industrial Aromatic Hydrocarbons, expresses acidity in terms of milligrams of sodium hydroxide consumed when 100 mL of sample are titrated using phenolphthalein indicator. If two drops or less of standard 0.1 *N* sodium hydroxide solution produce a persistent pink end point, the sample is reported to contain no free acid.

ASTM Method D 1613, Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products, expresses total acidity in terms of weight percent acetic acid or as milligrams of sodium hydroxide required to neutralize one gram of sample. The test is performed by mixing 50 mL of sample with an equal volume of water (or with an equal volume of alcohol if the sample is not water soluble) and titrating with aqueous 0.05 *N* sodium hydroxide solution to the phenolphthalein end point.

Acid Wash Color

ASTM Method D 848, Acid Wash Color of Industrial Aromatic Hydrocarbons, is a test used for benzene, toluene, xylenes, refined solvent naphthas, and similar aromatic hydrocarbons. Acid wash color is a measure of chemical reactivity of trace impurities rather than a measure of the color of the sample itself.

The test is performed by agitating a sample with sulfuric acid under prescribed conditions. The color of the acid layer is compared with colors of aqueous reference solutions containing various concentrations of cobalt chloride, ferric chloride, potassium chromate, and potassium dichromate. The color scale ranges from zero for distilled water to 14 for the darkest reference color standard. The color developed in the acid layer gives an indication of impurities in the aromatic hydrocarbon which if sulfonated would cause the material to be discolored.

Alkalinity

ASTM Method D 1614, Alkalinity in Acetone, specifically covers the determination in acetone of alkalinity calculated as ammonia (NH_3). The sample is added to an equal volume of water previously neutralized to the methyl red indicator end point. If alkalinity is detected, it is titrated with 0.05 *N* sulfuric acid and is reported as weight percent ammonia.

Benzene Content

Benzene is classed as a toxic and carcinogenic compound. A knowledge of the concentration of benzene may be an aid in evaluating the possible health hazards to persons handling and using solvents, but the ASTM test methods are not intended to evaluate such hazards. In addition, benzene content is an important specification requirement for aromatic hydrocarbons used as chemical intermediates.

ASTM Method D 4367, Benzene in Hydrocarbon Solvents by Gas Chromatography, may be used to determine benzene content of hydrocarbon solvents at levels from 0.01 to 1 vol%. An internal standard, methyl ethyl ketone (MEK), is added to the solvent sample, which is then introduced into a gas chromatograph equipped with two columns connected in series. The specimen passes first through a column packed with a nonpolar stationary liquid phase, methyl silicone, which separates components by boiling point. After octane has eluted, the flow through the nonpolar column is reversed, flushing out components higher boiling than octane. The octane and lighter components then pass through a column with a highly polar phase, 1,2,3-tris(2-cyanoethoxy)propane, which separates the aromatic and nonaromatic compounds. The eluted components are detected by a conventional detector and are recorded on a strip chart. Peak areas are measured, and the concentration of benzene is calculated by reference to the internal standard.

ASTM Method D 4534, Benzene Content of Cyclic Products by Gas Chromatography, applies to cyclohexane, toluene, individual C_8 aromatics, cumene, and styrene. Benzene may be determined over a range from 5 to 300 mg/kg (5 to 300 ppm). The test is performed with a gas chromatograph equipped with a flame ionization or other detector and a column containing a polar stationary liquid phase such as tetracyanoethylated pentaerythritol. A reproducible volume of sample is injected. Quantitative results are obtained from the measured area of the recorded benzene peak by using a factor obtained from the analysis of a blend of known benzene content.

Nonaromatic Hydrocarbons in Aromatics

ASTM Method D 2360, Trace Impurities in Monocyclic Aromatic Hydrocarbons by Gas Chromatography, covers the determination of total nonaromatic hydrocarbons and trace monocyclic aromatic hydrocarbons at levels of 0.0005 to 1 percent by weight in high-purity benzene, toluene, and mixed xylenes by gas chromatography. This inspection is of particular importance when these high-purity aromatics are used as chemical intermediates.

This test method is performed using an internal standard, *n*-butylbenzene, added to the specimen which is then introduced into a gas chromatographic column. The sample passes through the column, which contains a polyethylene glycol stationary liquid phase, and it is separated into nonaromatic and aromatic components. The components are detected by a flame ionization detector as they elute from the column and appear as peaks on the chromatogram. Peak areas are measured, and the concentration of the composite nonaromatics and each trace aromatic component is calculated with reference to the internal standard.

Nonvolatile Residue

ASTM Method D 1353, Nonvolatile Matter in Volatile Solvents for Use in Paint, Varnish, Lacquer, and Related Products, describes the analytical measurement of residual matter in solvents that are intended to be 100% volatile at 105 ± 5°C. Volatile solvents are used in the manufacture and application of paint, varnish, lacquer, and other related products, and the presence of any residue may affect the product quality or efficiency of the process.

Nonvolatile residues may consist of oil contamination, dissolved solids, rust, sand, or dirt. Trace oil contamination, which could cause cleaning solvents to leave an objectionable deposit of oily residue, often will not be detected by any other specification test.

This test is performed by evaporating to dryness 100 mL of solvent in a carefully cleaned, dried, and tared evaporating dish of platinum, aluminum, ceramic, or glass, first on a steam bath and then in an oven at 105 ± 5°C. Weight of any residue remaining in the dish is determined, and the result is reported as milligrams of nonvolatile residue per 100 mL.

Olefins Content

Olefins are undesirable impurities in hydrocarbon solvents. They are unsaturated, reactive compounds that tend to oxidize, causing solvent discoloration and objectionable noncharacteristic odor. The level of olefins present can be determined by reacting them with bromine. The amount of bromine that will react is a measure of the olefin content.

ASTM Method D 1159, Bromine Number of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration, is used for testing materials which have fairly high olefin contents. Bromine number is defined as the number of grams of bromine that will react with 100 g of sample.

The test is performed by first dissolving the hydrocarbon sample in a titration solvent composed of specified proportions of glacial acetic acid, carbon tetrachloride, methanol, sulfuric acid, and mercuric chloride. The dissolved sample is then titrated at 0 to 5°C with a bromide-bromate solution. (The titration is run at low temperature since addition of bromine to olefinic molecules proceeds rapidly and completely at temperatures down to or below 0°C, while competing reactions with aromatics and compounds of sulfur, nitrogen, or oxygen, if present, are minimized.) End point of the titration is indicated by a dead-stop electrometric titration apparatus. Bromine number is calculated from the weight of sample and from the volume of bromide-bromate reagent titrated. Values are generally in the range of 1 to 100.

Hydrocarbon solvents usually have a bromine number of less than one. Therefore, for greater accuracy, precision, and discrimination, it is more appropriate to use ASTM Method D 1492, Bromine Index of Aromatic Hydrocarbons by Coulometric Titration, or ASTM Method D 2710, Bromine Index of Petroleum Hydrocarbons by Electrometric Titration. Bromine index is defined as the number of *milligrams* of bromine consumed by 100 grams of sample (as compared with bromine number which is expressed as *grams* of bromine consumed by 100 grams of sample). Although the test procedures differ, bromine index is the more sensitive test and may be assumed to be numerically equal to 1000 times the bromine number.

In the coulometric titration method, the specimen is added to an electrolyte solution consisting of glacial acetic acid, methanol, potassium bromide, and mercuric acetate, and it is titrated with electrolytically generated bromine at room temperature. End point is determined by a dead-stop method when excess bromine is detected. The time of titration and generation current are proportional to the bromine generated and consumed by the sample.

Sulfur Content

Crude petroleum usually contains traces of sulfur compounds, the greater proportion of which are generally removed during refining since they might otherwise cause objectionable corrosive tendencies and foul odors in refined products such as hydrocarbon solvents. There are several test methods which directly measure sulfur content or which indicate their presence indirectly.

Copper Strip Corrosion

ASTM Method D 130, Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test, indicates the presence of corrosive compounds (such as sulfur compounds) in hydrocarbon solvents and other petroleum products by their effect on a highly polished test strip of copper. The polished copper strip is immersed in the solvent sample in a test tube and heated for 3 h at 100°C. At the end of this period, the copper strip is removed, washed, and compared with ASTM Copper Strip Corrosion Standards. Rating classifications range from "1a—slight tarnish," light orange, almost the same as the freshly polished strip, to "4c—corrosion," jet black.

ASTM Method D 849, Copper Corrosion of Industrial Aromatic Hydrocarbons, is similar to ASTM D 130 but applies specifically to aromatic hydrocarbons. The sample and polished copper strip are placed in a flask fitted with a condenser and are placed in a boiling water bath for 30 min. At the end

of this period, the copper strip is removed and compared with the ASTM Copper Strip Corrosion Standards. Aromatic solvents are reported to pass the test if the copper strip ratings are "1a" or "1b," indicating only "slight tarnish"; all other ratings are considered failures.

Doctor Test

The Doctor Test is a very sensitive qualitative test for detecting hydrogen sulfide and mercaptan sulfur in hydrocarbon solvent naphthas. It is described in section 6.1.10 of ASTM Specification D 235 for Mineral Spirits.

The test is performed by vigorously shaking together in a test tube the solvent being tested and an aqueous sodium plumbite solution. A small amount of pure, dry flowers of sulfur is added so that practically all of it floats on the interface between the solvent and the sodium plumbite solution after shaking. If the solvent is discolored or if the yellow color of the sulfur film is noticeably masked or discolored and blackened, the test is considered positive and the solvent is reported as "sour." If the solvent remains unchanged in color and the sulfur film is bright yellow or only slightly discolored with gray or flecked with black, the test is considered negative and the solvent is reported as "sweet."

Sulfur by Lamp Method

ASTM Method D 1266, Sulfur in Petroleum Products (Lamp Method), is used for quantitatively measuring total sulfur content of solvents. The sample is burned in a wick lamp in an artificial atmosphere of 70% carbon dioxide and 30% oxygen to prevent formation of nitrogen oxides. A solution of hydrogen peroxide is used to absorb the oxides of sulfur which are formed during combustion and to oxidize them to sulfuric acid. After flushing with air to remove dissolved carbon dioxide, the absorbent is titrated with a standard solution of sodium hydroxide. Sulfur is calculated as percent by weight from the weight of sample burned and the volume of sodium hydroxide reagent required to titrate the acid in the absorbent. Alternatively, the sample may be burned in air, in which case the sulfur as sulfate in the absorbent is reacted with barium chloride to precipitate barium sulfate, and the sulfur content is determined gravimetrically.

Trace Sulfur by Coulometry

ASTM Method D 3961, Trace Quantities of Sulfur in Liquid Aromatic Hydrocarbons by Oxidative Microcoulometry, is a highly sensitive quantitative test for the determination of sulfur content in the range of from 0.5 to 100 mg/kg (0.5 to 100 ppm). The test may be extended to higher sulfur concentrations by appropriate sample dilution. Although the test method applies specifically to aromatic hydrocarbons, it may also be used for other solvents.

The test is performed by injecting a measured liquid sample into a quartz combustion tube in an electric furnace maintained at about 800°C and having a flowing stream of gas consisting of about 80% oxygen and 20% inert gas. Oxidative pyrolysis converts the sulfur to sulfur dioxide which then flows into a titration cell where it reacts with triiodide ion present in the electrolyte.

$$I_3^- + SO_2 + H_2O \longrightarrow SO_3 + 3I^- + 2H^+$$

The triiodide thus consumed is coulometrically replaced.

$$3I^- \longrightarrow I_3^- + 2e^-$$

These microequivalents of triiodide generated are equal to the microequivalents of sulfur dioxide entering the titration cell. The sample result is compared with that of known calibration standards, and appropriate calculations are made to report the sulfur concentration.

Water Content

Dissolved water can have adverse effects on solvent end-use applications. For example, it can reduce solvency. Water can cause reactions with isocyanates during polyurethane preparation and with moisture-cure polyurethane paints and varnishes causing polymerization and gelation during storage. Metallic pigments can react with water to generate hydrogen gas, which can expand and burst paint cans. Dissolved water can act as a catalyst poison when a solvent is used as a reaction diluent for polyolefin polymerization.

Karl Fischer Reagent Method

ASTM Method D 1364, Water in Volatile Solvents (Fischer Reagent Titration Method), is a quantitative test. It is based on reactions involving the reduction of iodine by sulfur dioxide in the presence of water. These reactions can be used quantitatively when pyridine and an alcohol are present to react with the sulfur trioxide and hydroiodic acid produced in the reagent.

$$H_2O + I_2 + SO_2 + 3C_5H_5N \longrightarrow 2C_5H_5N{\cdot}HI + C_5H_5N{\cdot}SO_3$$

$$C_5H_5N{\cdot}SO_3 + ROH \longrightarrow C_5H_5N{\cdot}HSO_4R$$

To determine water content, Fischer reagent (a solution of iodine, pyridine, and sulfur dioxide in the molar ratio of 1:10:3) dissolved in anhydrous 2-methoxyethanol is added to a solution of the sample in anhydrous pyridine-ethylene glycol (1:4) until all water present has been consumed. This is evidenced colorimetrically by the persistence of an orange-red end-point color or electrometrically by an indication on a galvanometer or similar current-indicating device which records the depolarization of a pair of noble-metal electrodes. The reagent is standardized by titration of measured amounts of water.

Alternatively, automatic instruments are commercially available which operate on a coulometric principle according to ASTM Method E 1064, Water Content of Liquid Organic Chemicals by Coulometric Karl Fischer Titration. A measured quantity of sample is introduced into a titration cell containing reagent which undergoes the Karl Fischer reactions. Iodine is coulometrically regenerated, the amount of current required being proportional to the water content of the sample.

Heptane Miscibility Test

Oxygenated solvents are capable of dissolving sizable amounts of water. They can be checked qualitatively for water content by ASTM D 1476, Heptane Miscibility of Lacquer Solvents. Heptane is water immiscible and has a very low tolerance for water in solvent blends. The test is performed by mixing the solvent sample under test with heptane

in a 1:19 proportion and agitating. A clear solution indicates miscibility and low water content (less than about 0.5 wt%) in the solvent sample. A turbid solution indicates immiscibility and the presence of high water content in the solvent sample.

Water Solubility

Certain oxygenated solvents are completely miscible, e.g., methanol, isopropanol, acetone. This property can provide a qualitative means for indicating the presence or absence of water-insoluble contaminants, such as oils, paraffins, olefins, aromatics, high molecular weight alcohols, ketones, etc. Water-insoluble materials in the solvents may interfere with many of their end-uses.

ASTM Method D 1722, Water Miscibility of Water-Soluble Solvents, covers the determination of the miscibility of water-soluble solvents with water. The sample is diluted to 10 volumes of water in a glass graduated cylinder. The resulting mixture is viewed through the length of the column of liquid toward a dark background while being transversely illuminated. The sample is reported to pass the test if there is no evidence of cloudiness or turbidity initially and after 30 min.

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Part 6: Pigments

19

White Pigments

by Juergen H. Braun[1]

INTRODUCTION

ALMOST EVERYTHING MAN-MADE that is white or light in color contains white pigment in its surface: houses inside and outside, industrial articles, plastics, glazes, rubber, printed surfaces, many paper products, and even some foods. Only papers and textiles can be white without pigment.

Virtually all this whiteness and lightness is supplied by titanium dioxide (TiO_2) pigments. Void pigments make a minor contribution. The classic white pigments—lithopone, zinc sulfide, and the white leads—have essentially disappeared from commerce because TiO_2 pigments perform much better, are much cheaper, and are nontoxic. Zinc oxide is still added to some paints as a mildewstat, but not as a white pigment.

TiO_2 pigments are manufactured by a major, globally distributed industry. Its products are sold for many applications; however, more than half of all white pigment goes into paints. In many coatings, white pigment is the single most expensive ingredient. To select the right pigment grade and use it well is an important challenge to the paint manufacturer.

This chapter will familiarize coating manufacturers with white pigments and help them understand their options for selection, utilization, and testing. Toward this objective, I will first outline the commerce and manufacture of white pigments and then discuss their function, the substances that serve this function, and the commodities available. I will distinguish between product characteristics that describe the pigment itself and product performance, which are properties of paint films, that is, systems composed of pigment and binder.

Commerce

The white pigment market is served almost exclusively by titanium dioxide pigments. Globally, six billion pounds are produced annually at a value of six billion dollars. The value of TiO_2 pigments exceeds by far the combined value of all color pigments.

Five manufacturers share two thirds of the world market. Most of these producers operate several large plants located in industrialized countries. The largest of these plants makes about two million pounds of pigment a day. Their products are of similar quality. A few small plants operate in the lesser developed countries making the product at somewhat lower quality for regional consumption.

In the United States and other developed countries, one half of the TiO_2 pigment is used in coatings, one quarter in paper, and 15% in plastics. All other end uses, pigmentary (inks, floor coverings, elastomers, roofing granules, fibers, fabrics, sealants, foods, etc.) and nonpigmentary (ceramics, welding rods, etc.), account for the remaining 10%. In less developed countries, most of the TiO_2 pigments go into paints and plastics.

Manufacture

TiO_2 particles, the active ingredient of pigment, are made by two processes:

1. The old sulfate route dissolves the ore in sulfuric acid, purifies the aqueous solution of titanyl sulfate, precipitates a hydrous titania gel, and calcines the gel to crystallize it into aggregates of pigment particles, which, in turn, must be ground.
2. The newer, "greener" chloride route chlorinates the ore and purifies the $TiCl_4$ intermediate by distillation and chemical treatments. $TiCl_4$ is then flame oxidized to pigmentary TiO_2 particles and chlorine. The chlorine is recycled.

Sulfate processes are low-tech, labor-intensive operations in batch mode. Chloride processes are high-tech, automated, continuous operations. Sulfate and chloride products do not differ much in performance except that chloride TiO_2 is purer and thus brighter.

Waste disposal is a significant factor and constraint. The sulfate process generates vast quantities of dilute sulfuric acid and iron(II)sulfate from its ilmenite ($FeTiO_3$) ingredient.[2] The chloride process makes iron(III)chloride by-product in much lesser quantities that are dependent on ore composition: rutile (TiO_2), anatase (TiO_2), leucoxene (TiO_2/$FeTiO_3$), and ilmenite ($FeTiO_3$).

After the primary pigment particles are made by either process, their surfaces are treated to adapt the pigment to a variety of end uses. These treatments are carried out in aqueous suspension followed by drying, grinding, and dry treatment operations. Pigments are also converted into slurry grades.

[1]Consultant, 614 Loveville Road, Building E, Apartment 1-H, Hockessin, DE 19707-1616.

[2]The iron-free minerals, rutile and anatase, do not dissolve in sulfuric acid and cannot be used as such in sulfate processes.

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By either process, manufacture involves five steps:

1. Digestion of the ore.
2. Purification of the intermediate.
3. Crystallization of pigment particles.
4. Treatment of the pigment surface.
5. A variety of finishing operations.

Research and Development

For 50 years, the TiO_2 industry has been large, competitive, and profitable enough to dedicate sizable science and engineering resources to product improvement. These efforts have been remarkably successful. *Today's TiO_2 pigments are complex structures composed of an optically active core with shells that adapt the pigment to specific end uses.* Each feature is carefully designed into each pigment grade, optimizing it for its specific application. Their optical performance approaches the light-scattering effectiveness calculated from concepts of theoretical physics.

Experts in pigment technology, with the help of specialists in optics, surface chemistry, fine-particle technology, and chemistry have resolved many of the compromises between often conflicting requirements. End users can contribute to progress by suggesting new opportunities. Solving pigment problems does, however, require expertise in pigment technology.

THE FUNCTION OF PIGMENTS

Most coatings have two functions, aesthetic and protective. More often than not, manufactured surfaces are visually unattractive and therefore coated for aesthetic appeal. The coating hides the substrate's discolors and contrasts and provides a visually pleasing appearance or identification. Pigments[3] are not directly involved in the protective function of coatings.

Pigments supply the hiding and color of a coating. They are incorporated in surfaces to make them look bright or dark, colorful or drab, white or black, either more appealing or more appropriate to whatever the intended service. Toward that end, pigments must hide the unattractiveness of a substrate. Thus, pigments serve the human eye. They interact with visible light and cause surfaces to be seen in colors[4]: chromatic colors like red, blue, and green or achromatic colors like black, gray, and white.

To understand this primary aesthetic function of pigments, let us consider the interactions of visible light with matter at or near surfaces. Involved are two mechanisms of optics: light scattering and light absorption.

White or bright hiding is achieved by light scattering, an optical mechanism by which a ray of light is scattered as it hits an interface. White pigments are substances selected to scatter light very well.

Hiding also can be achieved by the absorption of light that is involved in colored and black surfaces and pigments. Optical absorption is decisively more efficient than optical scattering. Thus, less color or black than white pigment is required for hiding. Dark and black paint films can therefore be thinner than their white and light counterparts.[5]

Table 1 relates appearance characteristics of surfaces to the optical phenomena that cause them. If all light is absorbed by a surface, none scattered, the surface is perceived as black. If all light is scattered, none absorbed, the surface is seen as white. If a portion of the light is scattered and another portion absorbed, the surface is gray. If the absorption and scattering is wavelength dependent, for example, if red light is absorbed and green light is scattered, the surface is colored by the scattered green portion of the light. Even though common usage refers to objects as colored, i.e., red cars, green mountains, almost always only their surfaces matter.[6]

The return of light from a surface is caused by reflection at the surface and scattering from beneath with pigment causing the scattering. The optical action itself occurs at or in pigment particles, not on but within the surface. Light reflected at the surface does not usually change its color.[7]

Light scattered and returned from inside the coatings makes a surface look white or, if color pigments are involved, gives color to the surface. It is the white pigment in the coatings that does most of the light scattering.

Light scattering can be explained quantitatively from optical theories. Geometric optics give a graphic but superficial picture that accounts well for effects of refractive indices of potential pigments but unreliably for effects of pigment particle size. Wave optics and electromagnetic theory provide a more accurate but quite abstract model, accounting for particle size but not for effects of particle shape, orientation, and crowding.

The optimum particle size at which a population of white pigment particles scatters a maximum amount of light is about[8] 0.2 μm for green and white light. Blue light is scattered more efficiently by smaller particles, red light by larger ones. For pigments of high refractive indices, the theoretical curve of optical effectiveness versus particle size has a sharp peak (Fig. 1). For pigments of lower refractive indices, the peak broadens but the optimal size near 0.2 μm does not change much.

The pronounced wavelength dependence of optimum scattering causes a subtle color effect by white pigments in colored coatings. Their color shifts toward red if the white pigment is larger than optimal. Color shifts toward blue if the white pigment is smaller. This "undertone" is visible in col-

[3]Anticorrosive "pigments" do not meet Webster's definition of a pigment as "a substance that imparts black or white or color to other materials."

[4]In most technical contexts of color and colorants, white, gray, and black are considered colors.

[5]The transparency of white clothes, in particular wet, white clothes, illustrates the relative hiding effectiveness of white and color.

[6]This comes about because visible light and thus human vision penetrates pure gasses to a depth of about 10^{+6} m, pure liquids to about 10^{+2} m, dielectric solids to about 10^{-3} m, and metals to about 10^{-9} m, a range of 15 orders of magnitude.

[7]Exceptions are the colored metals—gold, copper, and their alloys—and extremely strong colorants, for example, copper phthalocyanine and hematite.

[8]The uncertainty is not in the optical calculation but reflects difficulties in defining the size of particles other then spheres. What, for example, is larger, a large snake or a small monkey? It depends on the perspective of the observer.

TABLE 1—Optics and appearance.

If the Pigment in the Coating		Then the Coating	
Absorbs Light	Scatters Light	Returns Light	And Looks
All	None	None	Black
None	All	All	White
Some	Some	Some	Gray
Some,in specific wave bands		Colored	

ored coatings and in white coatings at incomplete hiding. In gray coatings the effect can be quite obvious and at times objectionable.

Pigments can act by themselves but are usually used in combinations: white pigment with a small amount of color or black pigment, white pigment with one or more color pigments, combinations of color pigments, color pigments with some black pigment, etc. Some types of pigment particles scatter light, others absorb it. White pigments deliver white appearance by scattering all light (see Table 1). Black pigments absorb all light. Color pigments create color by absorption of light of specific wave bands. Sometimes, though, the wavelength-specific absorption by color pigments is augmented by wavelength-specific scattering.

Pigments, because they are particulates, can affect surface texture and texture-related appearance characteristics: gloss and sheen.

Pigments do the optical, that is, the aesthetic work; they provide the color and the hiding. Binder keeps the pigment on the substrate and does the mechanical and the chemical work that protects the substrate from the environment. The less effective the pigment in its optical function, the thicker the coating must be to hide and provide the desired color. Thick coatings, however, cost more than thin ones. Since the cost of binder increases proportionally to film thickness, film costs are inversely proportional to the effectiveness of the pigment. Economics discriminate severely against pigments of low optical effectiveness.

The economics of hiding are illustrated by Fig. 2, a plot of the cost of hiding as a function of pigment volume concentration for the case of a typical white paint applied to hide color contrasts of a substrate. The film is composed of a TiO_2 pigment at $1 per pound and a density of 4 g/mL dispersed in a resin at $1 per pound and a density of 1 g/mL. Hiding cost has a distinct minimum. At too low a pigment volume concentration, the film must be thick to hide. The cost of hiding increases because additional resin is required to deliver the film thickness. At too high a pigment volume concentration, the white pigment is used inefficiently, also increasing cost, albeit at a lower rate.

THE SUBSTANCE OF WHITE PIGMENT

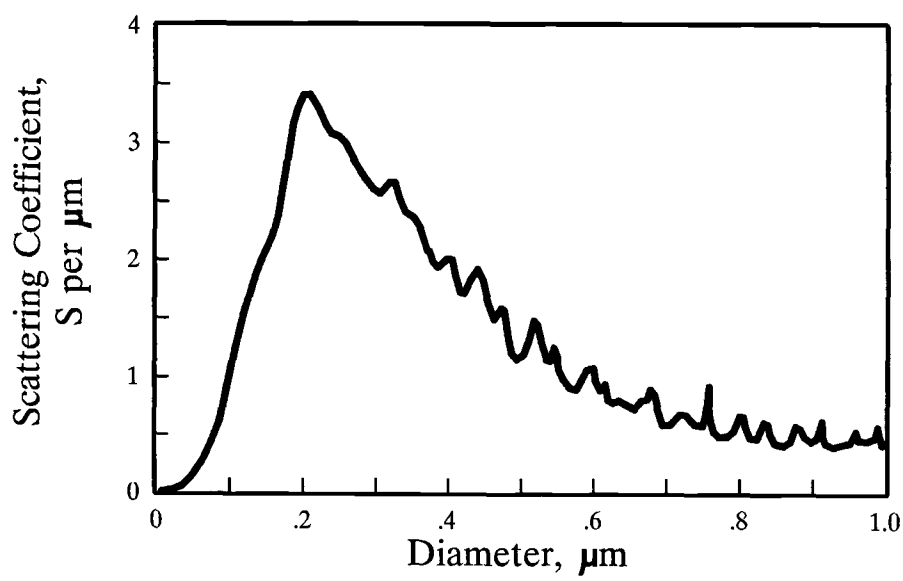
White pigments translate light scattering into hiding power, brightness, and opacity of thin films. The films, in turn, hide the color and contrasts of the substrate.

To serve as an effective white pigment, a substance must meet requirements that limit the selection to less than one dozen from among the thousands upon thousands of natural and man-made chemicals. A potential white pigment must:

- have an extremely high refractive index

In addition the substance must be:

- stable
- almost colorless
- suitable for manufacture in optimized, colloidal particle size
- a solid
- insoluble in water and organic solvents
- safe in manufacture, end use, and as a waste



Calculations: W. D. Ross, Du Pont Company

FIG. 1–Scattering by spheres of rutile in resin. From Braun, J. H., *Introduction to Pigments*, monograph in the Federation Series on Coatings Technology, Federation of Societies for Coatings Technology (United States), 1993.

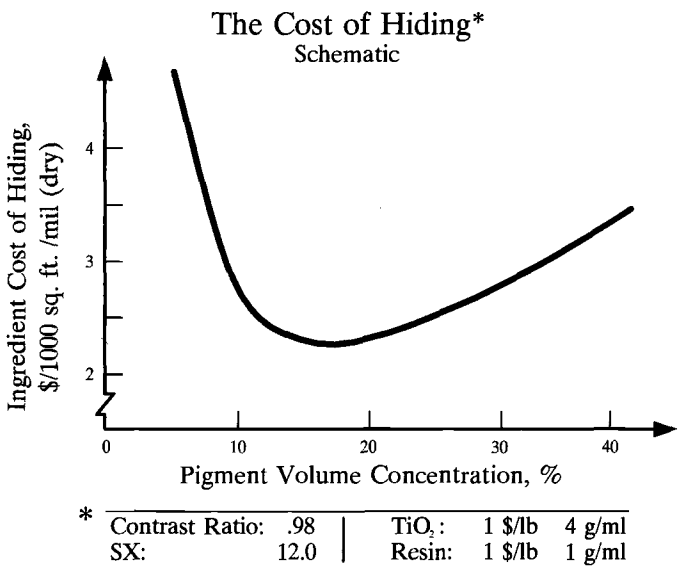


FIG. 2–The cost of hiding. From Braun, J. H., *Introduction to Pigments,* monograph in the Federation Series on Coatings Technology, Federation of Societies for Coatings Technology (United States), 1993.

Of these, the requirement of an extremely high refractive index, larger than 2.0, is essential and is most restrictive. Most materials with high refractive indices are hydrolytically unstable. A combined requirement for extreme refractive index plus stability eliminates all but a few substances.

High density is a disadvantage for a pigment. Pigments function by volume yet are sold by weight. Thus, a high-density pigment contains fewer particles per pound to do its optical work than a low-density pigment.

Because of its optical performance, safety, and cost, titanium dioxide has become the only white pigment of commercial significance. In the foreseeable future, it is quite unlikely that a better white pigment will be found to replace TiO_2 because its performance advantage results from a combination of a uniquely high refractive index with other essential characteristics.

TiO_2 has the highest refractive index of all ordinary, colorless, and stable substances, significantly higher even than diamond. Refractive indices of most compounds such as TiO_2 have been measured and can even be calculated from pure theory. No colorless substance, neither real nor hypothetical, has been found[9] that has a higher refractive index than TiO_2.

Before the commercialization of titanium dioxide, lithopone ($BaSO_4/ZnS$), zinc oxide, zinc sulfide, and white lead [lead(II)hydroxy carbonate] served as white pigments. All have lower refractive indices, scatter less effectively, and are much less cost effective.

Not only particulates but also air voids in coatings scatter light as if they were particles. But air voids are far less effective than TiO_2. Voids thus contribute to hiding but at direct or indirect costs. In coatings below their critical pigment volume concentration, voids scatter light and hide as such. But because they do not hide as well as TiO_2, films must be thicker, increasing binder cost. In coatings above the critical pigment volume concentration, extenders create a network of interconnected voids. These pores enhance the hiding effectiveness of the pigments. This indirect hiding contribution of voids is cheap to achieve in a paint but comes at the expense of mechanical and chemical film qualities. Pores (1) concentrate mechanical stresses to where they initiate fracture and (2) conduct aggressive chemicals from the surface into the depth of the paint film. The hiding improvements and the quality detriments of coatings above their critical pigment volume concentration can be quite large.

TiO_2 PIGMENTS

Titanium dioxide has obsoleted all other white pigments because TiO_2 is cheaper to use and much safer than other pigments. TiO_2 pigments are the most effective scatterers of visible light. They hide better and provide more lightness. They are more stable and less toxic.

Figures 3 and 4 show what TiO_2 pigments "look" like. Figure 3 is a transmission electron micrograph of an uncoated TiO_2 pigment grade dispersed in a dispersant by conventional techniques of grid preparation. Single crystals, twins, aggregates, and small agglomerates are visible. Weakly bonded agglomerates, though, are not distinguishable from strongly bonded aggregates because micrographs do not show strength of bonding. Figure 4 shows a set of electron scanning micrographs of dry pigment in bulk and as an individual floc. Visible are masses and individual crystallites, single and twinned. At highest magnification, scanning electron micros-

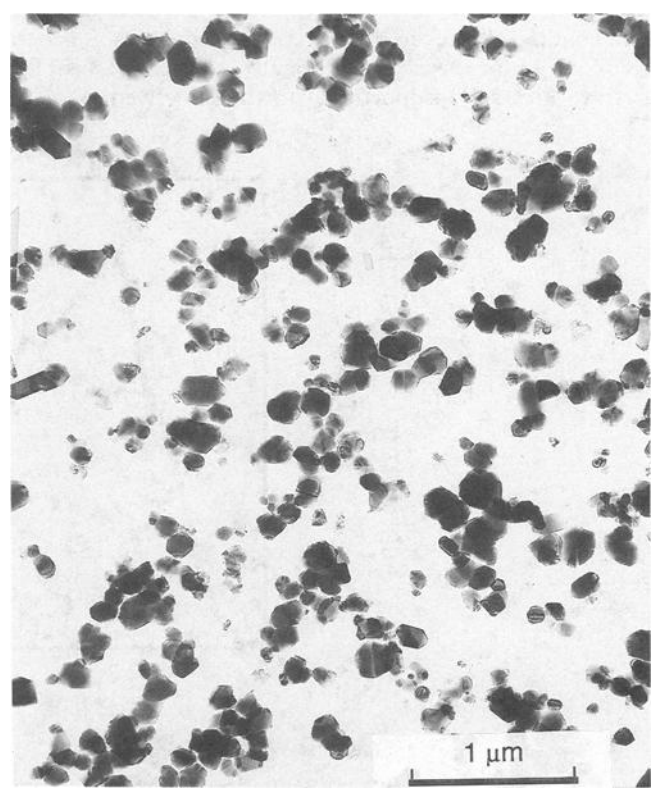


FIG. 3–Transmission electron micrograph of TiO_2 pigment.

[9]Extreme pressure phases of TiO_2 could be expected to have higher densities combined with higher refractive indices.

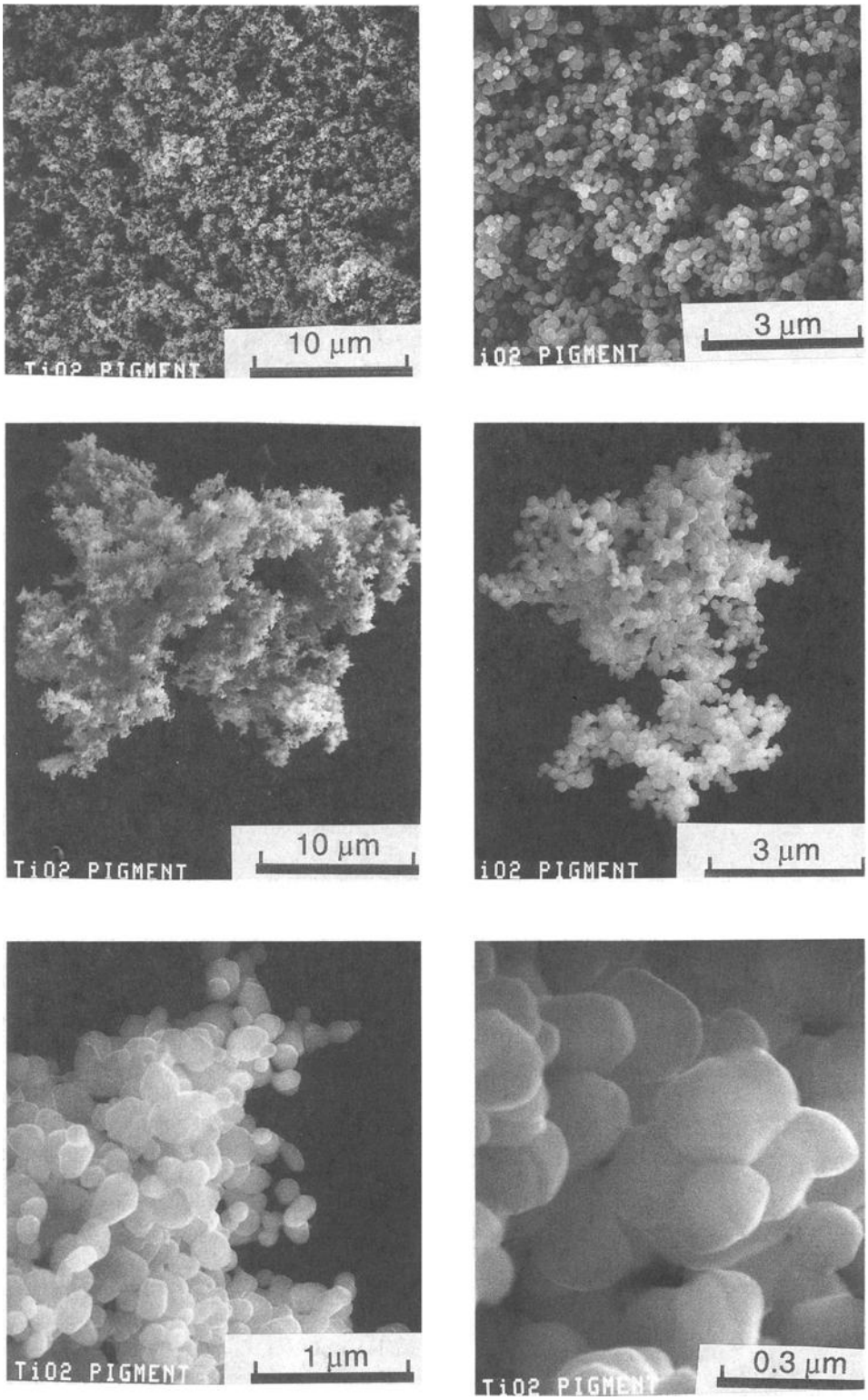


FIG. 4—Scanning electron micrographs of TiO_2 pigment.

copy shows crystals significantly more rounded than they actually are.

TiO_2 pigments are made in two crystal phases, rutile and anatase, that differ in lattice structures, refractive indices, and densities. Anatase was the first commercial titanium dioxide pigment but, for the coatings industry, has now been replaced by rutile because, in organic media, rutile has an 18% scattering advantage over anatase.

For the sake of clarity I will distinguish between characteristics and performance of a pigment. Composition, for example, is a characteristic of a pigment that is essentially independent of its environment. By contrast, hiding power

describes the performance of a system, a pigment within a paint film. Hiding is a film characteristic that depends on pigment volume concentration and a host of formulation and application parameters of the paint in which the pigment was evaluated.

Characteristics are properties of the commodity: composition, density, particle size, etc. They can be measured on the commodity, either dry powder or slurry. Granted, some product characteristics are affected by the ambiance in which they are measured but only in secondary ways. Particle size is an example of a characteristic affected by method of measurement.

At the state of the art it does not appear possible to establish rigid links between pigment characteristics and performance. Thus, the pigment commodity cannot be defined exclusively in terms of its characteristics. Certain characteristics can be measured reliably. Their results bear on but do not guarantee performance. Clearly, complete specifications for pigments must include both product characteristics as well as product performance measures.

A few generalizations of the connection between pigment characteristics and product performance are appropriate:

- High gloss pigments: (1) pack densely as indicated by measures of oil absorption, liquid demand, and interstitial space; (2) contain few agglomerates larger than about 0.5 μm[10]; and (3) have hydrous oxides contents that are low and TiO_2 contents that are correspondingly high [*1*].
- Pigments intended for high-pigment volume concentration paints contain up to 20 wt% hydrous oxides because fluffy oxides act as very efficient extenders. TiO_2 contents are correspondingly low.
- Satisfactory outdoor durability precludes the presence of more than about 1 wt% anatase phase with the rutile [*2*].
- Product fractions smaller than about 0.1 μm and larger than about 0.4 μm constitute losses to optical performance because particles that are too large or too small scatter light inefficiently.
- Impurity metal ions within the rutile crystals can degrade brightness dependent on the nature of the metal ion. Certain ions degrade color in concentrations as low as 0.000 01 wt%. Effects of ion contaminants on characteristics other than brightness are generally insignificant. Hydrous oxide coatings can tolerate a much higher concentration of impurity metal ions in the coating without much effect.
- Hydrous oxide coatings on pigment have ion-exchange characteristics. Their exchangeable ion content affects pigment performance in applications that are sensitive to pH (acid-catalyzed coatings) or the presence of electrolyte (electrocoatings).
- Pigment surface area affects oil absorption.

Some of these effects are sufficiently well quantified for translation into specifications.

Pigment Characteristics

TiO_2 pigment has to meet stringent specifications of crystal phase, particle size, surface characteristics, and purity. As with all chemicals, every product characteristic has some effect on every performance quality. Some specific characteristics, however, dictate equally specific performance attributes. These crucial relationships are described.

Refractive index and density are paramount to optical function, but they are not subject to manipulation. Crystal phase impacts weathering and light-scattering performance. Particle size controls light scattering and has effects on color. Surface characteristics are designed into the product through chemical treatments reflected by commodity composition. The treatments improve dispersibility, durability, and gloss performance. High purity of the pigment makes for brightness.

TiO_2 Crystallites

The active ingredients of a TiO_2 pigment commodity are its TiO_2 crystallites. Other components of the commodity affect the commodity density but do not affect the crystallite density nor the refractive index of the pigment. Neither the refractive index nor the density of any chemical can be manipulated independently by conventional technology.[11]

Two crystal phases of titanium dioxide serve as pigments: rutile and anatase. They differ in refractive indices, densities, and weathering performance because rutile and anatase differ by the arrangement of the titanium and oxygen ions within the crystals (Fig. 5). Rutile crystals are elongated, are denser, and have higher refractive indices.[12] Because of their higher refractive indices, rutile pigments scatter light more effectively than anatase products. They are also much less prone to chalk.

Rutile absorbs slightly more violet light than anatase and is slightly more yellow in bulk. However, little, if any, of this yellowness extends into pigment applications.

TiO_2 is a UV-energized oxidation catalyst of organic polymer. Anatase surface is about ten times more reactive than rutile surface. It takes only 10% anatase in rutile to reduce to one half the life expectancy of a paint film. Thus, for all exterior applications, the phase purity of rutile pigments is quite important.

During paint manufacture or usage, titanium dioxide cannot undergo transitions of crystal phase, that is, it cannot change its lattice structure. This contrasts to most organic pigments, many of which phase convert readily, usually with dramatic loss of optical performance. For example, an unstabilized α-copper phthalocyanine pigment, upon exposure to an aromatic solvent, grows into long needles of β-copper phthalocyanine, losing most of its color strength in the process.

Phase Analysis One percent or more of anatase in rutile pigment is considered undesirable because it increases the catalytic reactivity of the pigment. Fortunately, the phase analysis of TiO_2 pigment is cheap, convenient, and reliable.

Phase purity of pigment is usually measured by X-ray diffraction, for example, ASTM Test Method for the Ratio of Anatase to Rutile by X-ray Diffraction (D 3720-90). Conventional diffractometers can detect 1% of pigmentary anatase in 99% rutile by using peak intensity ratios or instrument

[10]Particle size measured as Stoke's settling diameters by sedimentation methods.

[11]Density and refractive indices of inorganic oxides can be increased together, but only at extreme pressures and astronomic cost.

[12]Actually, TiO_2 crystals have two principal refractive indices each. These two refractive indices do not differ much. They enter all relevant considerations of pigment as an appropriately weighted average.

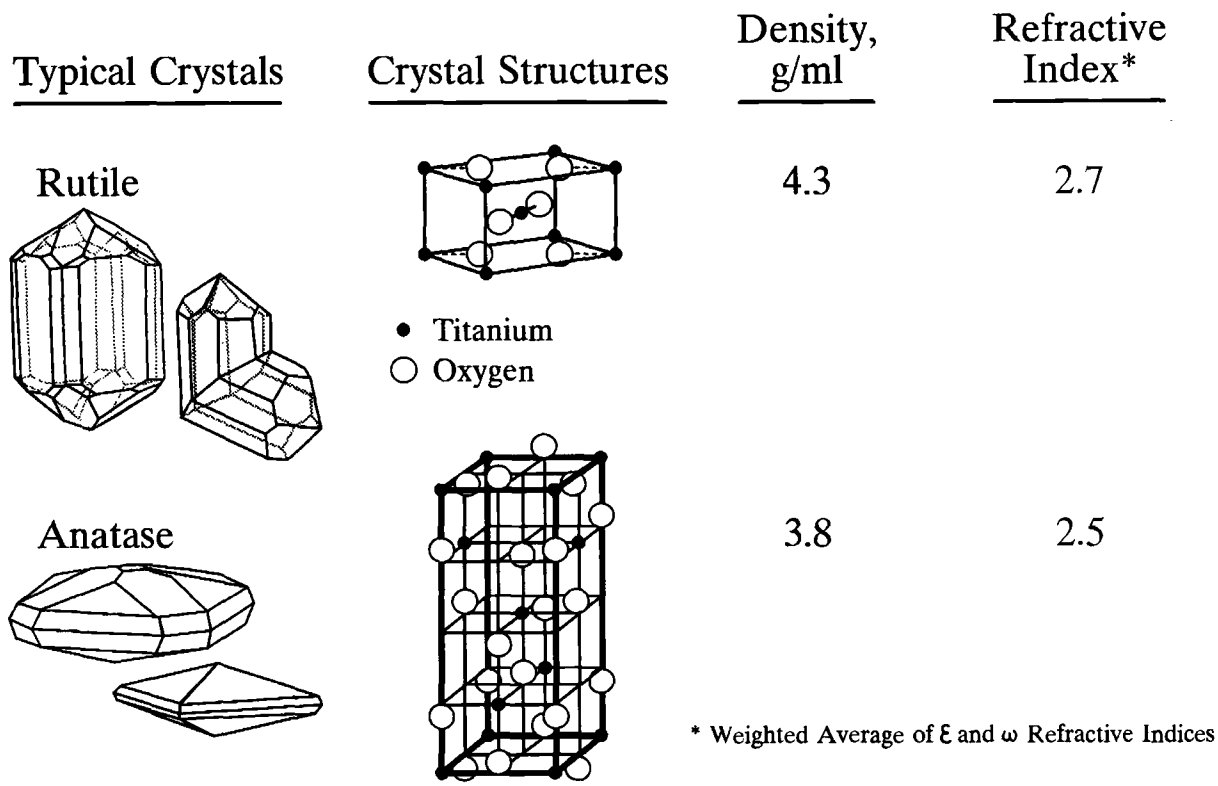


FIG. 5–Titanium dioxide crystals. From Braun, J. H., *Introduction to Pigments*, monograph in the Federation Series on Coatings Technology, Federation of Societies for Coatings Technology (United States), 1993.

counts. With careful attention to instrument alignment and sample preparation, a bit less anatase can be detected. Other, more complex techniques are more sensitive. However, why bother since less than 1 wt% anatase does not contribute much to the catalytic activity of the pigment.

The hydrous and anhydrous oxides contributed by pigment treatment are not detectable by X-ray diffraction because they are either truly amorphous or subcrystalline, that is, too small and/or too disorganized. Their diffraction lines are diffuse and drowned in the TiO_2 signal.

Pigment Particle Size

TiO_2 pigment particles are submicroscopic, so small that one pigment particle is to the size of a man as the size of a man is to the size of the earth. Thus, intuitive judgments based on macroscopic experiences are often misleading.

The particle size of pigment grades is tailored to the required optical performance. Pigment size depends critically on definition of "particle." For paint optics, the particle is the object a light beam meets in the paint film. Its size is a composite of primary particles, aggregates, agglomerates, flocs, and even of casual contact of any of these assemblies. Primary particles are individual single crystals and crystallographic twins.[13] They average from 0.1 to 0.3 μm in median diameter by weight with a geometric standard deviation of about 1.4.[14] Aggregates are associations of crystallites sharing grain boundaries and are thus strongly bonded. Agglomerates are associations of crystallites and aggregates bonded by relatively weak forces. Flocs are weakly bonded associations of crystallites, aggregates, and agglomerates formed spontaneously in a liquid or even in air.

The shear forces of paint application can disperse flocs. However, they are likely to reassociate. Paint grinding breaks most agglomerates if (1) the mill base is formulated to proper viscosity and (2) the mill is operated well. Aggregates can be broken only by high-intensity mills. Crystallites cannot ordinarily be broken. Aggregates and crystals, once broken, do not reassemble because aggregate bonding and crystal growth require thermal activation to many hundred degrees centigrade. TiO_2 pigments do not degrade in conventional paint and plastics processing.

The inclusion of casual contact in the definition of "particle" is important because it links size to concentration. At low pigment concentration, the frequency of particle overlap in a beam of light is low and the casual contact contribution to effective size is small. At high concentration, casual contacts are abundant and contribute significantly to the particle size as seen by a light beam penetrating a paint film.

Optimal scattering performance calls for optimal particle size. Particles that are too small in the extreme, molecular dispersions, scatter almost no light; particles too large, macroscopic crystals, are transparent. The particle size at which a population of TiO_2 particles scatters a maximum amount of light is about 0.2 μm for green[15] and white light. Blue light is scattered more effectively by particles closer to about 0.16

[13]Two or more single crystals intergrown according to some deducible law of symmetry.

[14]Geometric standard deviation = $\frac{1}{2}(D_{84}/D_{50} + D_{50}/D_{16})$, with D =

[15]For whiteness and brightness, green light matters most because

μm, red light by particles of about 0.23 μm. This optically effective particle size is likely to differ from the size measured by analysis.

Particle-size distributions of commercial TiO_2 pigments are narrower than those of many so-called monodisperse particulates (Fig. 6). Population statistics approach "log-normal" character, that is, a logarithmic transform converts the size distribution curve to "normal" (Gaussian) probabilities. Appropriately ground, pigment dispersions contain less than 5 wt% of particles smaller than 0.10 and larger than 1.0 μm. The mean particle size of pigment grades is tailored to the required light scattering performance. Pigment grades composed of small particles are made for applications at low-pigment volume concentration.

The pronounced wavelength dependence of optimum scattering causes a subtle color effect caused by white pigments in colored coatings. Their color shifts toward red if the white pigment is larger than optimal or toward blue if the white pigment is smaller. This "undertone" is visible only in gray and colored coatings and in white at incomplete hiding. In gray coatings the effect can be quite obvious, sometimes objectionable, sometimes desirable. Small size TiO_2 grades with blue undertone are used to make colors look "cleaner," i.e., less yellowish.[16]

Large particles in a paint film are detrimental to gloss. Thus, the coarse tail of the size distribution of TiO_2 pigments impacts gloss performance [*1*]. Figure 7 shows what particle size range impacts which performance characteristic.

Paint grind gages reveal the presence of minute quantities of grit, clumps composed of tens of thousands of primary particles. Grind gages do not respond to pigmentary particle sizes. For TiO_2 pigments, the presence of grit has no detectable optical effects.

Particle size control is one of the manufacturing secrets of the TiO_2 industry. Additives and process conditions during crystallization and grinding operations are crucial to particle size and product performance in both chloride and sulfate processes.

Particle Size Analysis—Up front a warning: *Particle-size analysis and the interpretation of analytical data calls for specialized expertise.* Potential pitfalls are so numerous that serious misinterpretation is the rule rather than the exception, particularly in the interpretation of electron micrographs.

Problems arise in several ways. Two definitions of "particle," be it clump, agglomerate, aggregate, or crystallite, are vitally important: (1) the particle of the analysis and (2) the particle that matters within the intended application. The analytical particle is almost never the same as the particle in a paint film that interacts with light:

- Dispersion is a true grinding operation that reduces particle size. In spite of this, grinding must be an integral part of the analytical procedure. Otherwise, the softest and largest clumps become valid members of population statistics.
- In sample preparation, dispersive work expended upon minute samples can add up to enormous energy concentrations that can break crystallites that cannot be broken en masse.

[16]Because dirt is colored by iron and thus reddish gray, a reddish or yellowish cast is perceived as "dirty."

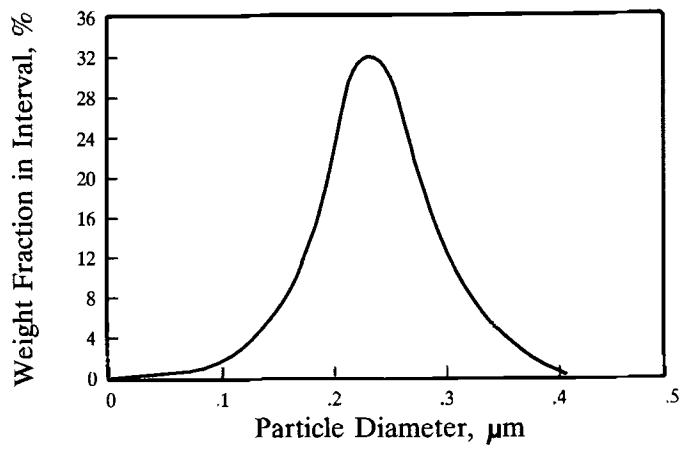


FIG. 6–Particle size distribution of TiO_2 pigment. From Braun, J. H., *Introduction to Pigments,* monograph in the Federation Series on Coatings Technology, Federation of Societies for Coatings Technology (United States), 1993.

- Sampling statistics is a frequent problem considering small quantities or low concentrations of pigment in samples.
- In microscopy, transmission images bear little resemblance to ordinary visual perceptions based on observation of surfaces. Scanning micrographs, by contrast, correspond to human vision. Differences become apparent when comparing Figs. 3 and 4.
- In light-scattering methods, the extreme refractive index of TiO_2 affects computational interpretation.
- No certified standards are available pertaining to the size range of pigments.

Numerous methods have been used for the size analysis of pigments: Andreasan pipette, disk centrifuges, transmission electron microscopy, light-scattering measurements, field flow fractionation, etc. They are too complex and far too costly for routine analysis.

Lately two methods have advanced TiO_2 technology because reproducible results can be obtained routinely: X-ray sedimentation and the X-ray disk centrifuge. Both are usually combined with ultrasonic dispersion.

X-ray sedimentation measures the Stokes' diameters of particles settling in water by gravity. Settling causes density differences in the suspension that are detected by absorption of X-rays. Brownian motion interferes with settling and distorts the small end of the size distribution curve of the particle population. The X-ray disk centrifuge substitutes centrifugal force for gravity, thus avoiding misrepresentation of small particle fractions.

Commodity Composition

The TiO_2 in the pigment is its optically active ingredient. Other components adapt it to its end use. The commercial products have compositions that fall into one of three categories: (1) uncoated pigments, (2) coated pigments, and (3) slurries.

Uncoated pigments contain 98% or more titanium dioxide; some contain up to about 1% aluminum oxide (anhydrous), and other products contain less than about 0.5% aluminum oxide with some other inorganic, anhydrous oxides. Organic additives and their decomposition products may be present

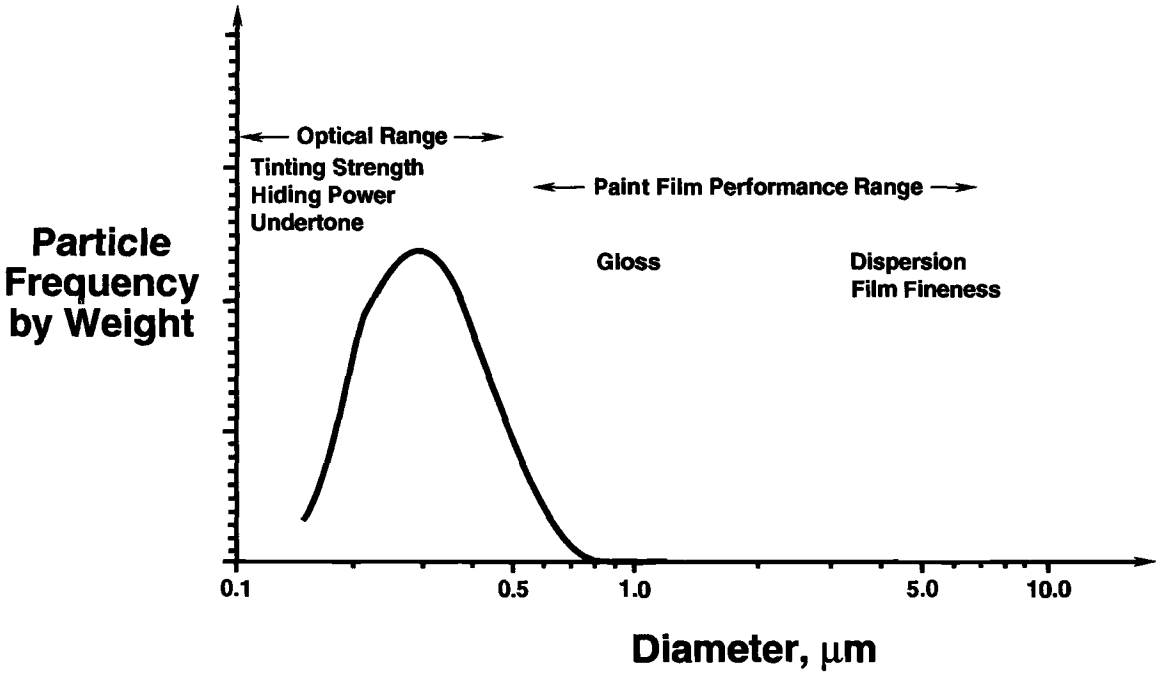


FIG. 7–TiO_2 aggregate size distribution. From Braun, J. H. and Fields, D. P., "Gloss of Paint Films, II," *Journal of Coatings Technology*, Vol. 66, No. 828, 1994, p. 93.

in concentrations of fractional weight percents. Uncoated pigments are used in plastics and paper. In coatings, wet-treated pigments are preferred because they are easier to disperse into liquids of low or moderate viscosity.

Minor constituents, either carried over from the ore or added in the manufacturing process, can be important in determining pigmentary properties because they can control crystallite size. Sulfate pigments retain up to 0.3% niobium pentoxide and 0.3% phosphorus pentoxide from the ore. They also contain up to 0.2% alumina, added to compensate for the presence of niobium. Compensation minimizes discoloration by the semiconductor imbalance that pentavalent and trivalent cations can cause in the rutile lattice.

Chloride process pigments contain practically no unwanted impurities because the titanium tetrachloride intermediate can be purified effectively. They contain about 1% pyrogenic alumina added for better process control and for photochemical stability improvement.

Trace constituents are generally unimportant except for transition metals such as iron, chromium, vanadium, etc., which degrade color by semiconductor mechanisms.

Besides inorganic constituents, most uncoated and many coated pigments contain up to 0.5% of an organic grinding aid to improve flow in the fluid energy mill to achieve a more uniform grind. The grinding aids are usually polyhydroxyl compounds (for example, trimethylol propane, triethanolamine, etc.) that can undergo some pyrolytic degradation in the mill.

For use in coatings, i.e., to be dispersible by the conventional paint-making equipment, TiO_2 pigments are "coated." In aqueous suspension, hydrous aluminum oxides are precipitated onto the surfaces of pigment particles. Interior grades contain a coating of up to 5% hydrous alumina for ease of dispersion. Durable grades have another coating that usually consists of about 2% silica and sometimes also oxides of zirconium, boron, zinc, cerium, and tin, usually in concentrations of less than 1%.

Rutile pigments are made suitable for extreme exposure by encapsulating individual particles in glassy silica sheaths. Silica surface treatments on TiO_2 pigments were once considered detrimental to gloss performance. Silica on pigment, however, comes in two distinct modifications, either "fluffy" or "dense." Fluffy silica does indeed reduce gloss and is precipitated onto pigments intended for dry hiding paints to increase oil absorption. Dense silica is used to encapsulate the TiO_2 particle in a distinct shell to make the pigment durable in severe exposure.

Special high oil absorption products are made for paints formulated for dry flat hiding, that is, above the critical pigment volume concentration. They contain fluffy coatings, 5 to 15% hydrous silica and 2 to 6% hydrous alumina, for better spacing and improved optical efficiency in vehicle-starved formulations. The fluffy silica increases oil absorption and water demand by the pigment. Gloss is reduced.

Slurry products for coatings applications are usually based on coated pigments. In addition to the coated product, they contain organic dispersants and stabilizers. Predispersed pigments, sold as aqueous slurries, contain from 60 to almost 80% titanium dioxide by weight. They are stabilized with low concentrations of organic chemicals.

Odorless amines are added for pH control. Together with preservatives, about 1% of organic material is present. Pigment loading in slurry is limited by the concentration at which the slurry becomes too thick to be pumped. Slurries of lightly treated grades are available at higher solids contents than slurries of heavily treated, dry flat grades. The slurries can be shear thickening. Effects can be severe.

The pigment industry describes its products and the hydrous oxides they contain in terms of their analytical equivalents, alumina (Al_2O_3), silica (SiO_2), and water (H_2O) or mois-

ture content. Such description does not imply structure or chemical characteristis of the components but reflects analytical results. The actual components of pigment coatings are hydrous oxides: boehmite (γ-AlOOH), diaspor (α-AlOOH), hydrargillite [γ-$Al(OH)_3$], etc.

Product descriptions in terms of analytical results are preferred because they can be verified. By contrast, the precise structural analysis of colloidal coatings on pigment surfaces is always difficult and often beyond the capability of even the most sophisticated analytical techniques. Results are usually ambiguous. But because coatings are precipitated from aqueous solution, the alumina coatings on coated TiO_2 pigments contain structural water, i.e., they are hydrous.

Wet treatments have profound effects on dispersibility and durability. In dry hiding paints, they affect hiding through oil absorption and spacing. Brightness is not usually affected.

Process details of wet treatment are guarded secrets of the TiO_2 industry. The patent literature provides little guidance because the most and least effective processes can be described by equally factual performance claims.

Elemental Analysis—Chemical analysis of pigments presents no particular problems. The quality of the data meets the requirements of pigment and coatings technologies. For routine analyses, conventional, wet analytical methods, for example, ASTM Test Methods for Chemical Analysis of White Titanium Pigments (D 1394-76), have been replaced by instrumental techniques for cost savings, not data quality. Aluminum and silicon contents are usually determined by X-ray fluorescence techniques. Water content is analyzed as weight loss of volatiles by thermogravimetric analysis (TGA).

Pigment Surface

Because pigment particles are so very small, their surfaces are enormously large. One pound of untreated TiO_2 has a surface of about one acre. Thus, surface characteristics have a profound impact on a pigment's interactions with all the other components of paints. Furthermore, pigment surfaces are complex composites reflecting the nature of the commodity.

The rutile component of most TiO_2 pigments contributes 0 to 10 m^2/g of surface area. Inorganic treatments with hydrous aluminas and silicas can more than double the total surface area of a pigment. Most pigment surfaces are composites of Ti—O, Ti—OH, Al—O, and Al—OH groups. Many pigment surfaces include Si—O and Si—OH units. Silica-encapsulated grades have few if any Ti—O and Ti—OH surfaces.

The surface areas themselves are not homogeneous. Usually they are composites to which TiO_2 contributes 0 to 10 m^2/g TiO_2 and 5 to 10 m^2/g pigment, hydrous aluminas with about 200 m^2/g $Al_2O_3 \cdot xH_2O$ and 2 to 8 m^2/g pigment, silicic acid with about 150 m^2/g $SiO_2 \cdot xH_2O$ and 0 to 10 m^2/g pigment, silica glass 5 to 10 m^2/g SiO_2 and 5 to 10 m^2/g pigment, etc. The chemical and physical characteristics of the surface are specific to the component. Granted, the components share important similarities. They are all hydrophilic oxides with high-energy surfaces.

Even the surfaces of titanium dioxide crystallites themselves are not just composed of titanium and oxygen ions. In the sulfate process, while the rutile crystallites grow, insoluble components accumulate on their surfaces. Those components are either impurities present in the ore and not removed in the purification process or additives designed to control crystal structure and growth and to regulate agglomeration. This fortuitous surface is not necessarily suitable for a given end-use application; thus, crystallite surfaces are modified by treatments.

The surfaces of TiO_2 pigments are wetted readily. They are usually hydrophilic and disperse spontaneously into water. The energy of wetting is high, aiding dispersion into organic liquids. The ease of wetting of TiO_2 pigments contrasts with wetting problems of organic color pigments, most of which are hydrophobic and have a low negative free energy of wetting. Water does not wet them without the help of surfactants. Suitable organic solvents may wet organic pigments but often only sluggishly.

Since unmodified pigments tend to cake and flow poorly, they are treated with up to 0.5% of a grinding aid, usually organic polyhydroxyl compounds, to improve dry flow. These organic materials remain on the pigment surface. Silicone treatment can be used to make dry pigment flow like sand, but the pigment becomes hydrophobic and unsuitable for most coatings applications.

Surface Analyses—Surface analysis of pigments involves three interrelated subjects: surface area, surface composition, and surface chemistry. For data interpretation, sample density data are also required. Methods and results tend to be more interesting to the scientist than the practitioner.

Instrumental surface area determinations are now routine. Nitrogen adsorption is used widely. Reliability of results is satisfactory. Data are affected by the composite character of pigments and its response to sample preparation.

The modern methods of surface analysis, Microprobe, ESCA, etc., have been used to study pigment surfaces and have yielded interesting results and valuable insights. Costs and technical complexity preclude their widespread and routine uses.

Surface adsorption by pigments has been explored extensively by surface calorimetry and in terms of adsorption isotherms, etc. Ambiguities introduced by the composite character of the surfaces have their impacts.

The density of a pigment can be measured precisely and quickly by a helium densitometer. However, for fine powders of known composition, calculated densities are often more reliable than measured values. Density calculation requires knowledge of the pigment composition and the density data for the pure component oxides. It is decisively important to include in the calculation the total water content: absorbed moisture plus the structural water of the hydrous oxides.

Pigment Packing

The packing density of pigment particles affects paint film performance. This density is an inverse measure of interstitial volume, a reflection of the way pigment particles aggregate and agglomerate into either stringy assemblies that haystack loosely or compact clumps that pack densely.

Effects of packing density on performance are profound. Packing characteristics determine the critical pigment volume concentration of a pigment. Through the critical pigment volume concentration, pigment packing affects virtually all characteristics of paint films [*3*]. Fluffy pigments have

a low critical pigment volume concentration; particulates that pack densely have high critical pigment volume concentrations. In effect, the critical pigment volume concentration itself is a measure of the interstitial volume of wetted pigment particles. Adsorption layers are also involved, but in most instances their contribution is minor.

Practitioners of coatings technology have long been aware of the importance of packing. They used oil absorption of a pigment as one of its most important descriptors. Oil absorption is still used today because it reveals so much about the pigment even though linseed oil has lost its importance as a binder.

Oil absorption is primarily a measure of wet packing complicated by the involvement of adsorption layers, dispersion work, and flocculation. The measure predates the insights of Asbeck/Van Loo into structure and performance of paint films.[17] Thus, the connection between oil absorption—the practical measure—and the scientific concept—critical pigment volume concentrations—is unnecessarily convoluted. Oil absorption of different pigments cannot be compared because the measure is based on weights, not volumes. Critical pigment volume concentration, by contrast, is based on volumes and lends itself readily to comparisons of particulates that differ in densities.

At its best, when oil absorptions of similar pigments of identical densities are measured by an experienced individual who uses a standardized procedure to his personal end point, oil absorption values become a reasonably precise measure of the packing of pigment particles in oil.

For wetted particles, pigment packing is not affected much by the nature of the liquid, water, oil, or solvent provided the particles are not flocculated. In practice, surfactants must be added or be present as a natural component of the system as it is in raw linseed oil. "Liquid absorption" values agree pretty well with each other if they are based on relative volumes of a pigment in a variety of liquids.

Incidentally, oil absorption values correlate inversely with the bulk density of a given pigment. The fluffier the pigment packs in air, the more loosely it packs in liquids.

Packing Measures—In spite of its many shortcomings, oil absorption is the only measure of packing that is widely accepted. The test is a titration of raw linseed oil into dry pigment powder to an end point at which the mass cakes. Two procedures are in common use: ASTM Test Method for Oil Absorption of Pigments by Spatula Rub-out (D 281-84), and ASTM Test Method for Oil Absortion of Pigments by Gardner-Coleman Method (D 1483-84).

Precision of oil absorption data is poor unless all measurements in the data set are made by one experienced individual. For tests by different laboratories, the spatula method has a coefficient of variation of 12%, with 5.3% for the Gardner-Coleman method. Data obtained by two analysts tend to differ because the end point of the titration is more difficult to define than to reproduce.

[17]Asbeck and Van Loo recognized that the characteristics of paint films involve volume rather than weight considerations, no small matter when densities of paint film components can range from 0.9 to 6 g/mL.

Contaminants

Extraneous metal ions within rutile crystallites can degrade the brightness of pigment. Nickel and chromium can be detrimental in concentrations as low as a few parts per million. Involved are semiconductor mechanisms. Substitution of extraneous ions for Ti^{4+} in the TiO_2 lattices discolors the crystals usually towards gray or yellow.

Impurities and co-products introduced by the treatment chemicals are far less detrimental to brightness. Co-products can, however, affect specialized performance requirements. Certain ions can, for example, inhibit cure of acid or base-catalyzed coatings or cause film defects in electrocoatings.

Purity and brightness of TiO_2 crystallites are process related. TiO_2 crystallites made by the chloride process are purer and brighter than sulfate products.

The co-product content of a pigment commodity is usually not a matter of poor operating practice but set by complex compromises between conflicting performance requirements.

Trace Analyses—Trace impurities in pigments are analyzed by conventional emission spectroscopic and X-ray fluorescence methods. Results are considered reliable though not particularly precise.

Color

Titanium dioxide is a virtually colorless dielectric with some semiconductor characteristics due to small amounts of contaminants. Rutile absorbs in the violet end of the visible spectrum. Figure 8 shows schematically the reflectances of

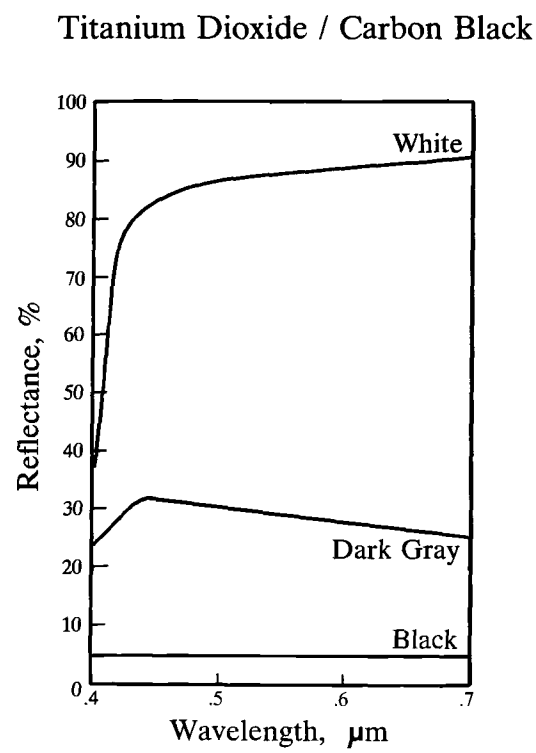


FIG. 8–Reflectances of white, gray, and black paints. From Braun, J. H., *Introduction to Pigments*, monograph in the Federation Series on Coatings Technology, Federation of Societies for Coatings Technology (United States), 1993.

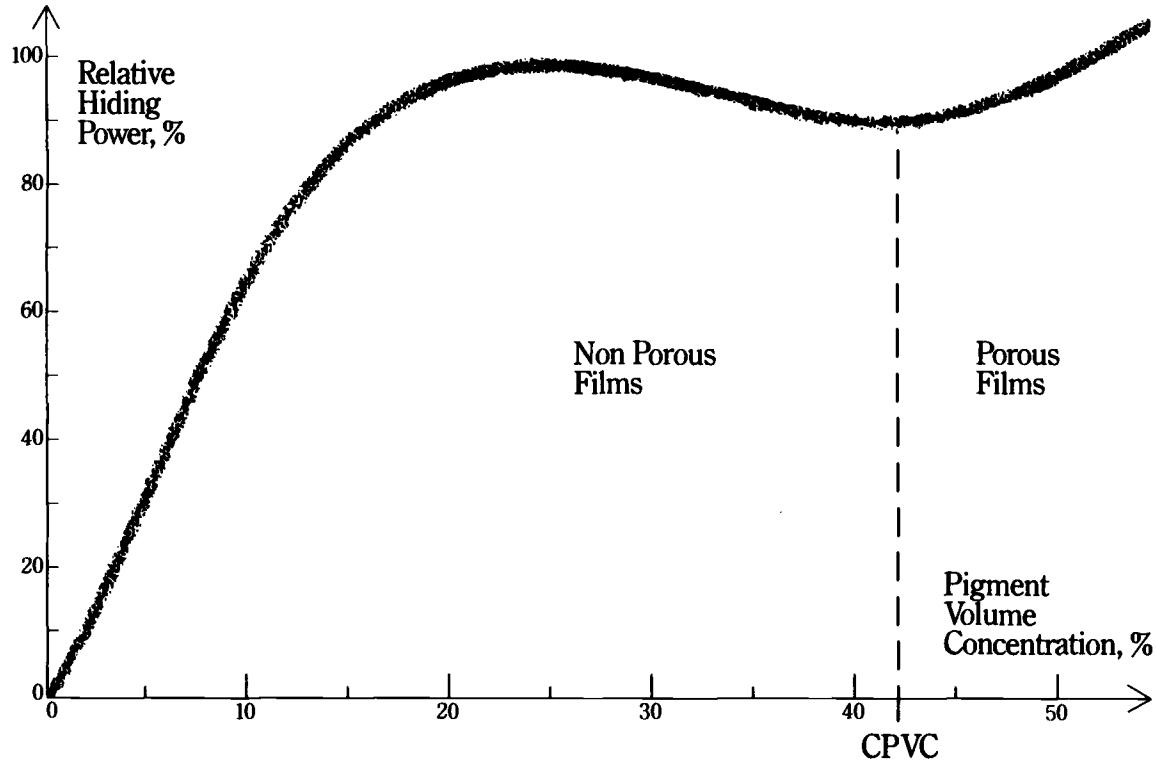


FIG. 9–Hiding power of paint films. From Braun, J. H., *Introduction to Pigments*, monograph in the Federation Series on Coatings Technology, Federation of Societies for Coatings Technology (United States), 1993.

white, gray, and black paints pigmented with only TiO_2, with TiO_2 and carbon black, and with only carbon black, respectively. Absorption of far violet light imparts a slight yellow hue to large crystals. The anatase absorption edge is at a shorter wavelength than rutile, shifted almost completely into UV wave lengths. Thus, anatase crystals are slightly less yellow. All this does not matter much in coatings. For high-purity pigment, dry powder color does not correlate with end use color because most polymers contribute far more yellowness than the pigment.

Pigment brightness matters less in most coatings applications than one might presume. Most coatings, even white ones, are toned, that is, their brightness is reduced intentionally by addition of carbon black or color pigments. Purity, thus brightness, is important only for white coatings that are usually not toned: coatings for light fixtures, many coil coatings, most inks, and ink-similar paints.

Chloride process pigments are intrinsically brighter and whiter than their sulfate counterparts. Typically, chloride process pigments average 99.5% L*[18] lightness,[19] and 98.5% sulfate pigments.[20] The difference between chloride and sulfate pigments, an L* lightness difference of 1%, is about ten times larger than the least visible difference.

TiO_2 particle size has a significant effect on the color of tinted coatings and thin white films. Smaller particles scatter blue light more efficiently. As a result, pigment of a smaller average particle size will shade bluer both tinted coatings and white coatings at incomplete hiding. Pigment of larger average particle size will shade redder in the same systems. Most TiO_2 grades for coatings applications are neutral in this particle-size-related undertone. Products intended for very low end-use concentrations are often bluish. Red undertone pigments are not in demand.

Color Measurement—Color measurements of pigment are performed on dry pressed pellets. Modern spectrophotometers provide data with more than sufficient precision for most purposes of pigment quality control. Most of these instruments can report their results in any of several color coordinates. The L*a*b*[21] system seems particularly well suited to describe variations on the theme of white.

Hazards

TiO_2 pigment is a benign chemical. Its hazards, and the relative lack thereof, are detailed in Material Safety Data Sheets that must accompany any U.S. shipment. TiO_2 presents no pronounced health hazards; it is neither corrosive nor acutely toxic and does not appear to be a significant carcinogen nor embryo toxin in the workplace. As a dry powder, TiO_2 can become a nuisance dust that may require control.

TiO_2 pigment cannot burn nor explode, neither as a dry powder nor as aqueous slurry. Neither the dry pigment nor the slurry is corrosive nor reactive. The hazards of pigment

[18]CIELAB (Commision International de l'Eclairage, 1978) metric of lightness.

[19]Brightness/lightness of a dry pressed pigment pellet.

[20]In very first approximation, a TiO_2 pigment with an L* lightness of 98.5% contains a three times higher concentration of colorant impurities than a pigment of 99.5% brightness: 1.5%/0.5% = 3.

[21]CIELAB (Commision International de l'Eclairage, 1978) metric of color.

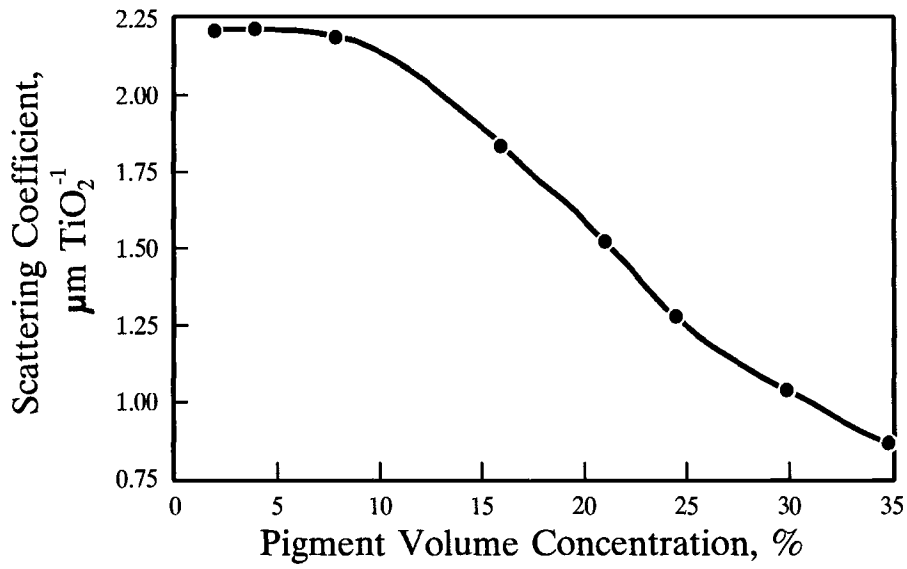


FIG. 10–Scattering coefficient of TiO_2 [4]. From Bruehlman, R. J., Thomas, L. W., and Gonick, E., "Effect of Particle Size and Pigment Volume Concentration on Hiding Power of Titanium Dioxide," *Official Digest*, Vol. 33, No. 433, 1961, p. 252.

dispersions in organic liquids reflect the characteristics of the liquids.

Pigment Performance

The TiO_2 industry sells light scattering for the price of TiO_2 because there is no better and cheaper way to achieve effective hiding by thin films that are white or light in color. Thus, optical effectiveness is the primary performance characteristic of the pigment. However, TiO_2 pigment is well optimized and functions near its theoretical potential. Between products developed for similar end use, light scattering differences are too small to matter or be measured. Thus, secondary performance characteristics can be commercially decisive.

Hiding and Opacity

Pigment sells by weight but scatters light, that is, functions, by its volume. The particle size of TiO_2 for white pigment applications was optimized for the scattering of visible light, first experimentally, later confirmed by theory. Commercial grades perform near theoretical potential. A rutile particle of about 0.2 μm diameter is optimal for green light, the wave lengths of greatest sensitivity of the human eye.

Figure 1 illustrates the relationship between scattering power and particle diameter. The Mie theory can specify the optimal diameter for the scattering of an electromagnetic wave by a dielectric particle with great precision, but the result is limited to single spheres. This complex and abstract theory must be translated (1) from a sphere into a real particle of elongated, angular shape, (2) from a single, isolated particle to assemblies of massive numbers, and (3) from mono-size particles to particle-size distributions. The task is formidable, yet significant progress has already been made.

Figure 9 illustrates the effects of pigment concentration on hiding a paint film. At first, hiding increases in direct proportion to concentration. Then, the crowding of pigment particles causes the increase to diminish, to reach a maximum, and to decrease toward the critical pigment volume concentration. Beyond the critical pigment volume concentration, dry hiding, that is, light scattering at air/pigment interfaces, causes hiding to increase again.

Crowding of pigment particles diminishes light scattering substantially [4] (Fig. 10). Effects become apparent at pigment volume concentrations above about 8 vol%. More than half of a pigment's scattering effectiveness can be lost between 8 vol% and the critical pigment volume concentration. A simple optical model explains the effects [5]. Improvements in pigment effectiveness achieved through control of crowding are likely to be fairly insignificant [6].

The optics within paint films are quantified by the Kubelka-Munk theory that combines for thin films the effects of light scattering (usually by white pigment) and light absorption (usually by color pigment). The model serves exceedingly well in spite of some theoretical limitations. Kubelka-Munk equations provide a basis or an explanation for most performance measurements: hiding, opacity, and tinting strength.

Measurements of Light Scattering—Until recently, pigments and paint films were evaluated by visual comparisons, for example, ASTM Test Method for Relative Tinting Strength of White Pigments by Visual Observation (D 332-87). The eye was more sensitive than available instruments, and the mathematics of Kubelka-Munk was too complex for routine calculations.

Two developments make quantitative evaluation of pigments now appropriate: (1) optical instruments have become more sensitive and more reliable than the eye, and (2) the least of computers can calculate results on the spot.

Light scattering and light absorption of paint films can be quantified independently using light reflectance or transmission measurements of thin[22] films drawn over black and white substrates. In addition, film thickness or film weight and composition must be measured. ASTM Test Method for Hiding Power of Paints by Reflectometer (D 2805-88), describes such a test.

[22]Thin enough to show obvious contrast between regions drawn over black and white backgrounds but thick enough to look uniform rather than mottled.

Relatively cheap and very reliable spectrophotometers can measure reflectances in any specific and narrow wave band. By measurements, wave band by wave band across the spectrum of visible light, applicability of hiding power measurements is extended from black and white to color. Paints of different hues can be compared and results expressed separately for performances of white and color pigments. Computer programs are available for data evaluation.

Tinting strength tests, ASTM Test Method of Relative Tinting Strength of White Pigments by Reflectance Measurement (D 2745-89), measure the relative light scattering of a white pigment by overwhelming the slight intrinsic absorptions of binder and pigment with a massive absorption by a standardized addition of colorant. Measured are thick films of infinite hiding.[23] The same test serves for the evaluation of color pigment. Here, the slight intrinsic scattering of the color pigment is drowned by the massive scattering from standardized addition of a white pigment.

Absorption of light within the paint film increases the hiding power of the film. The effect is quite pronounced. It can be caused by pigment or binder. When caused by a TiO_2 pigment of low brightness, this low-purity product can get undeserved credit for a hiding power advantage over purer products. Also, off-color extenders and colored polymers can boost hiding power incidentally or deliberately. This hiding improvement comes at the expense of brightness.

Dispersibility

To make a paint, dry powder has to be distributed in liquid composed of binder and solvent. The process is called dispersion or paint grinding.

The ease with which a powder can be dispersed in a liquid depends primarily on its particle size. As pigments go, TiO_2 at 0.2 μm size is large and easy to disperse, almost as easy as extenders, much easier than most color pigments. For all but glossy coatings, TiO_2 can be stirred into liquids with high-speed agitators. High-gloss finishes require more powerful equipment: media, roll, or ball mills.

Dispersing involves four distinct stages during which most of the energy of grinding converts to heat:

1. *Liquid replaces air-solid interfaces with liquid-solid interfaces.*

   The ease of wetting depends on (a) energy characteristics of the surface of the solid and (b) the chemical affinity between solid and liquid. TiO_2's high-energy surface wets well. By contrast, the low-energy surfaces of organic color pigments wet only with difficulty.

2. *Bonds between particles are broken.*

   TiO_2 crystals are not broken in ordinary mills. Bonds *between* crystals range in strength from strong within aggregates to weak within agglomerates. Weak aggregates can be broken in the high-energy mills of pigment and plastics technologies, not, though, by equipment common in coating technology. Agglomerates break in high-speed dispersers.

3. *Particles are distributed throughout the liquid.*

   The more viscous the liquid, the more power is required to mix and distribute and the more effective the grind.

4. *The distribution of particles has to be stabilized against reversible flocculation.*

   Nonaqueous systems flocculate by Brownian motion and are stabilized against flocculation by surfactants that provide steric hindrance. Aqueous dispersions flocculate by: (1) electrostatic attraction and by (2) Brownian collisions. They are charge stabilized by ionic dispersants.

Rheology matters decisively. Grinding in a shear-thickening rheology regime, dilatent grinding, is highly effective. By contrast, shear-thinning rheology of the grind charge absorbs energy into reversible bonding, wasting much of it as heat. High viscosity helps the energy transfer from mill to particulate. Thus, other parameters equal, grinding "viscous" is more effective than grinding "thin," and grinding "well cooled" is more effective than grinding "hot."

Flocculation degrades optical performance. White pigments can lose only a moderate fraction of hiding, rarely as much as 30%. By contrast, color pigments can lose most of their color.

Excessive or inappropriate grinding does not degrade TiO_2. Nor does optical performance improve with grinding because most of the pigment is dispersed very early in the grind cycle. A few parts per million of undispersed grit, however, can degrade film fineness from "excellent" to "inadequate."

Measurement of Dispersibility—This author knows of no reliable and useful measurement of dispersibility. Granted, it is possible to use standardized procedures to establish a ranking of pigment samples against specific performance requirements. Such a ranking cannot be quantified and does not translate from one application to the other.

In one such scheme, a paint is made by a minutely standardized, low-shear dispersion procedure. The paint is then tested for grit by one of several conventional fineness gages.

The "residual grit" aspect of dispersion is usually evaluated by fineness-of-dispersion gages, for example, ASTM Fineness of Dispersion of Pigment-Vehicle Systems (Method D 1270). The gages are shallow, tapered channels precision machined into steel blocks. A paint sample is scraped into the channel. The surface of the paint wedge is then examined to see at what depth the diameters of largest agglomerates exceed the depth of the channel. This point is visible as a transition from smooth to streaked paint surface.

Pigment Effects on Paint Film Durability

Durability is the continuance of decorative and protective performance of paint films and their components under the influence of weathering. Lack of weathering resistance manifests itself as: (1) oxidation of polymer ultimately to carbon dioxide and water; (2) discoloration and fading of color pigments; and (3) chalking of the TiO_2 with concomitant erosion and gloss loss. Instability of substrates introduces additional degradation effects.

For paint films with TiO_2, concerns involve the weathering resistance of the films themselves. Exposure to sunlight, moisture, and oxygen changes the appearance of paint films. Some films chalk and eventually erode to their substrates; others discolor and fade well before chalking becomes a problem.

[23]Thick enough so that a further increase in thickness does not affect reflectance.

Degradation of coatings occurs because paint films are slowly oxidized by air. Sunlight triggers the degradation reactions. In the dark, paint films can last for centuries, even millennia. In light, durability depends on binders, pigments, and the conditions of exposure. High humidity, particularly condensation, aggravates degradation.

Only the ultraviolet (UV) portion of sunlight causes degradation directly because it has an energy content sufficient to break chemical bonds. The degradation of UV-A and UV-B light[24] is irreversible for polymers and for all organic and some inorganic pigments. A few inorganic pigments are thermodynamically stable. Titanium dioxide is stable, but its catalytic characteristics are activated by UV above 3.08 eV. In effect, the band gap of TiO_2[25] is within the energy levels present in sunlight. All white pigments share some of this attribute. Extenders are stable and inert. Their band gaps are too large to be activated by the UV components of sunlight.

Titanium dioxide affects the durability of paint films in two distinct and opposing ways: (1) As a strong UV absorber, TiO_2 protects the paint film, and (2) as an UV-activated oxidation catalyst, TiO_2 degrades binders [7].

Three characteristics of TiO_2 are functionally disparate but are manifestations of a single fundamental characteristic of dielectric matter: (1) its unique refractive index, which makes TiO_2 the best white pigment; (2) its extreme UV absorptivity; and (3) UV catalytic activity of the TiO_2 surface.

Light of more than 3.08 eV, water, and oxygen are all essential for the TiO_2-catalyzed degradation of binder. Their reactions combine into a cycle that generates two free radicals from each active UV photon [8].

$$H_2O + O_2 + h\nu_{(UV)} \xrightarrow{TiO_2} \cdot OH + \cdot HO_2$$

The hydroxyl and peroxyl free radicals are highly reactive agents that oxidize and thus degrade essentially any organic polymer

$$2 \cdot HO + 2 \cdot HO_2 + CH_4 \longrightarrow CO_2 + 4\,H_2O$$

The chain of chalking events is cyclic with respect to TiO_2 and can be disrupted by exclusion of either UV, water, or oxygen.

Durability Control—The TiO_2 industry inhibits the catalytic activity of the TiO_2 surface and improves the weathering resistance of its products by encapsulation in amorphous silica. The shell is a true silica glass precipitated from aqueous solution by technology invented by DuPont in the 1960s [9]. Encapsulation of TiO_2 made it practical to paint cars in white and bright colors. Meanwhile, binders were improved to that less effective deactivation of the TiO_2's catalytic activity suffices for satisfactory performance of automotive finishes in temperate climates.

The SiO_2 glass prevents contact between the catalytic surface of rutile and the organic vehicle and provides a surface for recombination of free radicals. Figure 11 shows particles of a super-durable pigment. Their silica sheaths are barely visible on the transmission electron micrograph. The silica sheaths, themselves, after the TiO_2 was dissolved out, are shown in the transmission electron micrographs of Fig. 12. Even the holes are visible through which the rutile cores were dissolved.

Intermediate levels of weathering resistance are attained by partial encapsulation of the rutile in silica and/or alumina with or without zirconia and by bulky coatings of hydrous aluminum and silicon oxides on rutile.

Alternate approaches to chalking control are less effective or cause performance problems in coating applications. They involve attempts to: (1) recombine holes and electrons at the TiO_2 surface by semiconductor mechanisms whereby the products are slightly yellow; and (2) prevent the hydroxylation of the TiO_2 surface, i.e., interfere with one step of the chalking sequence, causing products to be gritty.

Durability Testing—Durability of coatings can neither be measured nor be predicted quantitatively. The best state-of-the-art technology can do is rank coatings. Cost per sample are exorbitant, precision is poor, and the time lag is prohibitive for many purposes. Years of outdoor or months of accelerated exposure are required for the pigment and binder combinations for which durability is important, that is, for durable pigment in durable binder.

Testing is done by simulation of a "real" world. Paints are made from experimental pigment and usually several pigment standards. Panels are painted. They are exposed where weathering is severe but is not necessarily representative of the intended application. Certain appearance characteristics are measured regularly and often: chalk, color, gloss, etc. Finally, data are reduced, correlated, and compared. Repro-

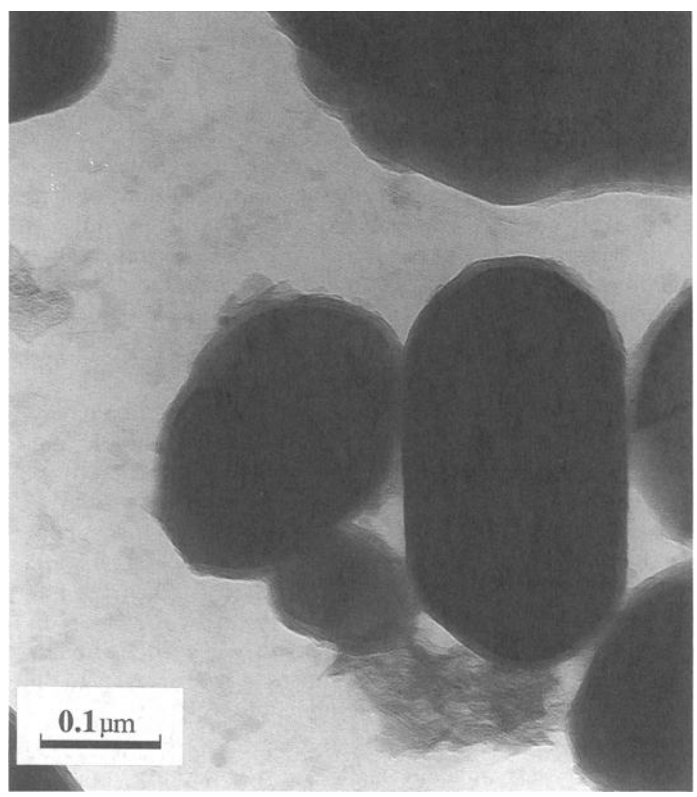


FIG. 11–Encapsulated TiO_2 pigment.

[24]UV-A is the UV wave length region near to visible light, UV-B is the medium UV region, and UV-C is the far (shortest wave length) UV light. Sunlight contains little UV-B and essentially no UV-C.

[25]The band gap is the "forbidden" energy gap between the valence band and the conduction band of a semiconductor. In the language of physics: "UV light induces semiconductor characteristics in TiO_2"; in the language of chemistry: "UV light reduces colorless TiO_2 to black Ti_2O_3."

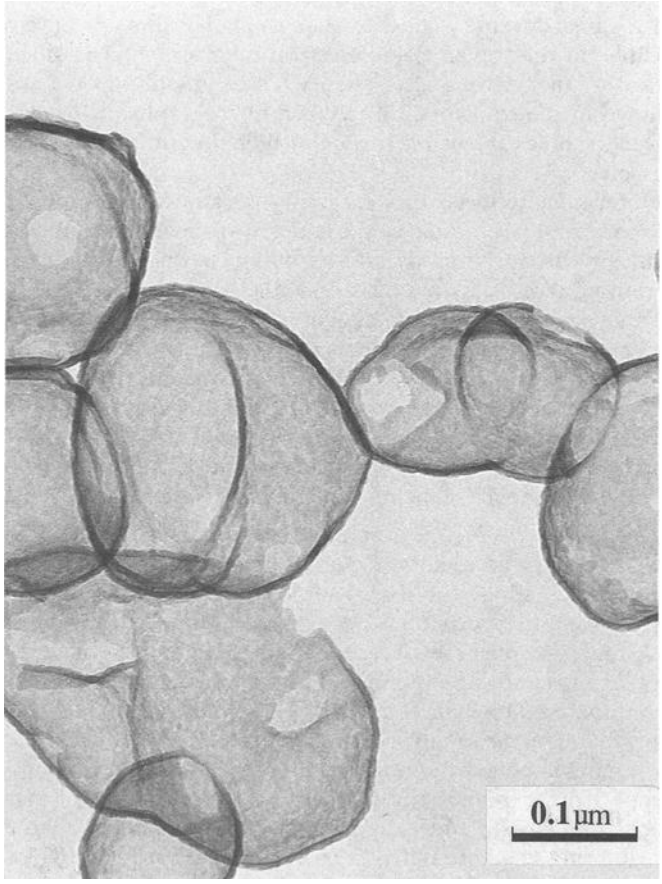


FIG. 12–Silica shells from encapsulated pigment.

ducibility is barely sufficient to tell an interior grade pigment from a durable grade without testing replicates. Experimental durability differences within grades are not generally detectable [*10*].

Results from one binder system cannot be extrapolated quantitatively to binders involving different polymer chemistry, nor can a single acceleration factor predict outdoor performance from accelerated exposures [*11*].

Pigment manufacturers supplement their exposure testing by science-based analyses of the catalytic activity of the pigment.

Pigment Effects on Gloss

Powders do not have a gloss; only surfaces can be glossy. Within surfaces, particulates affect gloss, for example, pigments in paint films. They are detrimental, particularly to the dimension of gloss perceived by the human eye.

Naturally glossy surfaces occur on liquids and amorphous solids.[26] Particulates in paint film, pigments, extenders, and some additives reduce gloss because they roughen the film surface. The more particulate is in the film, the lower its gloss. Clear paint films are glossy if they are thick enough. Thin films can telegraph the roughness of the substrate to the surface of the paint film, reducing its gloss.

Since the volume concentration of white pigments in paint films must be much higher for hiding than the concentration of color pigments and black, the burden of improvement falls on TiO_2 producers. They have increased gloss performance of grades that serve the automotive and industrial markets.

Gloss matters are complicated because a fundamental difference exists between the measured gloss that guides coatings formulation and the perceived gloss that sells cars [*1*]. These two operational definitions of gloss, one based on instrumental measurement of an *intensity of image* and the other on the human perception of a *distinctness of image,* differ profoundly in substance. However, they correlate well enough to guide quality control and pigment development by incremental improvement. The fundamental difference between measured and perceived gloss can, however, misdirect the strategy of product development, for example, a focus on increasing the refractive index.

A mechanism by which pigment causes the surface roughness that degrades gloss explains [*1*] that pigments diminish gloss by an interplay between the surface tension of the wet film with the compressive strength of a particulate bed and a gel structure that develops within the film while it cures. While the film is fluid, surface tension maintains the surface at a molecular smoothness that results in "perfect" intensity-of-image gloss. As the film dries, the structure within the wet film strengthens until it overcomes the surface tension that maintains gloss. Shrinkage of the partially cured film continues, but now shrinkage becomes uneven on a microscopic scale because only the binder/solvent combination, not the pigment, shrinks. Thus, micro-roughness develops and diminished gloss.

Gloss Measurement—Gloss measurement has long been routine: ASTM Test Method for Specular Gloss (D 523). Many conventional gloss meters are on the market. Most perform well for coatings pigmented with white and color pigments.[27] They come with measuring heads for three specular angles, generally 20, 60, and 85°. High-gloss surfaces are best measured at low (20°) specular angle, medium glosses at medium angle, and matte surfaces at grazing angle (85°). The selection of the proper specular angle improves instrumental precision.

The conventional gloss meters measure the intensity of light reflected by a surface, the intensity-of-image component of gloss. The human eye, by contrast, perceives the distinctness-of-image component of gloss. Thus, haze and so-called distinctness-of-image[28] data are used to supplement the conventional gloss measurements.

Compatibility

Usually, TiO_2 is used in combination with other pigments. Interactions between pigments can occur and are detrimental to performance. Often, hiding is decreased, color strength is lost, and chroma is reduced; occasionally, the hue shifts slightly.

Most interaction problems involve surface chemistry. The immediate cause of the problem is flocculation. Either the

[26]Single crystals are an exception, but their surfaces are small. Glass is an amorphous solid. Polished surfaces are not "natural." Incidentally, only liquids, amorphous solids, and single crystals can be transparent.

[27]For coatings that contain flake pigments, the interpretation of angle-dependent reflectance measurements is complicated.

[28]The distinctness-of-image instrument is really an intensity-of-image meter sensitized towards distinctness of image.

white or one of the color pigments has flocculated. Almost inevitably, the color pigment is at fault.

Most color pigments enter the market as toners, lakes, or dispersions, that is, complex composites that can contain more surfactants and modifiers than colorant. These additives are chemically reactive and can interact detrimentally with the surfactants or additives of the paint formula. Dry TiO_2 pigments,[29] by contrast, contain no surfactants and are inert and chemically less complex with far fewer possibilities of adverse interactions.

Chemical interactions between pigments are problems of the past caused by reactive pigments. White lead, for example, was incompatible with TiO_2 because UV exposure could cause gross, though temporary, discoloration. Few modern pigments are susceptible to these problems.

Problems between TiO_2 pigment and resins or additives do, however, occur occasionally because many paint films contain much higher concentrations of TiO_2 than of additives or of color pigments. Components of TiO_2 pigment can thus have significant leverage even if present in relatively small concentrations on the pigment. Problems are usually quite specific to the paint formula. Several such problems have been recognized and are resolved through specialized TiO_2 grades made, for example, for electrocoating primers and for acid-catalyzed paints.

Product Types

ASTM D 476-84 distinguishes four types of TiO_2 pigments (Table 2): one anatase type and three rutiles: interior, exterior, and pigment for paints formulated above the critical pigment volume concentration. The standard was formulated in 1939 with two classes of pigments. In the years since, the design of pigments has progressed to where the coatings industry can now select the most suitable pigment grade for a specific application from far more than two or four TiO_2 types. Granted, a single TiO_2 grade could serve diverse needs but would do so only moderately well. Optimal performance in any application demands specialized pigment grades that satisfy specific requirements of optics, surface chemistry, and dispersion technology. Some of these requirements can be met only through compromise.

The diversity of products can be described in terms of four specific performance dimensions: durability, gloss, dispersibility, and undertone. Then there are products aimed at specific applications: enamel paints, dry hiding paints, pigment slurries, acid-catalyzed coatings, electrocoated primers, etc. Finally, pigment grades are designed for the specific requirements of whole industries: coatings, plastics, paper, and ink.

These are the products designed to specific performance dimensions in coatings:

- *Durability:* Interior—Exterior—Severe Exposure

  Interior grades are unfit for exterior applications except when used underneath top coatings that absorb all light of wavelengths below 400 nm. All-purpose pigments are exterior durable in appropriately durable vehicles at moderate severity of exposure and for moderate appearance requirements. Severe exposure grades are intended for satisfactory performance including high gloss at exceptionally severe conditions, for example, at the horizontal position in the humid subtropics.

  Durability must be manufactured into the pigment surface.

- *Gloss:* Conventional—Flashy

  Conventional pigments satisfy the gloss requirements of most architectural and trade-sales applications and of many industrial coatings. High-gloss pigments are aimed at automotive and some flashy industrial finishes.

  High-gloss application call for pigments of small agglomerate size and low oil absorption.

- *Dispersibility:* Conventional—Low Shear

  Conventional pigments are designed to be dispersed by equipment developing moderate to high shear[30]: media mills, ball mills, roller mills, and high-speed dissolvers at low rates of throughput. Special pigments are available for low-shear, high-rate dispersion by high-speed dissolvers and for stir-in with screening.

  Dispersibility is promoted by surface treatments at some detriment to gloss.

  Unlike many color pigments, TiO_2 pigments are dispersible enough not to require predispersion.

- *Undertone:* Neutral—Blue

  In coatings applications, the undertone of the pigment, blue, neutral, or red, is rarely an issue. Thus, most coating grades have a neutral undertone. Blue undertone pigments are preferred in applications at very low pigment volume concentration. Red undertone pigments do not appear to be in demand.

  Undertone is affected by pigment volume concentration and controlled by the size of the primary TiO_2 particle, small for blue, intermediate for neutral, and large for red.

There are also specific coatings applications addressed by special product designs.

- *Grades intended for coatings below the critical pigment volume concentration.*

  Most TiO_2 pigments, conventional interior and exterior grades, conventional and high-gloss products, conventional and low-shear dispersible pigments, the neutral and blue undertone pigments, are all suitable for applications below the critical pigment volume concentration.

- *Grades intended for applications above the critical pigment volume concentration.*

  Heavily treated, low-gloss products perform better in dry-hiding paints than grades made for high and moderate gloss. In effect, the pigment contains its own, exceptionally effective extender.

- *Slurries intended for waterborne paints.*

  Aqueous slurries are suited only for waterborne applications. The costs of dispersion operations are borne by pigment manufacturers. For medium- and large-scale operations, savings from the elimination of a process step outweigh the costs of slurry-handling facilities.

- *Other specialized grades are made as opportunities are recognized and solutions developed.*

[29]Slurry grades do contain some organic surfactant.

[30]High shear within coatings technology. The plastics industry uses several more powerful mills.

TABLE 2—Excerpt from ASTM Standard D 476-84: Specification for titanium dioxide pigments.

	Type I	Type II	Type III	Type IV
	Anatase	Rutile		Rutile
	Free chalking	Medium chalk resistant		Highly chalk resistant
Typical Application	White exterior house paints; interior use	Low-medium PVC enamels and lacquers	Medium-high PVC enamels; alkyd and emulsion flat wall paints	Exterior coatings requiring excellent durability and gloss retention
TiO_2, min, %	94	92	80	80

Finally, industries other than coatings are targeted by specific products:

- *Plastics*

  Plastics are pigmented by products most of which are optimized for performance at PVCs of less than 1 vol%. Durability and dry-flow characteristics can be important to the plastics industry. High-gloss and low-shear dispersibility are usually not required.
- *Paper*

  The wet-end stage of paper making uses aqueous slurries. Slurry handling and optics are important; low-shear dispersibility, high gloss, and durability are not important.
- *Ink*

  Inks require pigments that are high in gloss. Compatibility with a wide range of solvents and vehicles is often important.
- *Miscellaneous end uses*

  Pigmentary applications (floor coverings, elastomers, roofing granules, fibers, fabrics, sealants, food additives, etc.) and nonpigmentary applications where pigment is used for its TiO_2 content (ceramics, welding rods, etc.) or as a low-cost, mono-disperse particulate (for example, as catalyst support).

Also, the same products can be packaged in different ways, bag, semi-bulk, or bulk, or analyzed for special purposes, for example, food additive purity. Each such product may enter commerce under its own grade designation.

The wrong grade of TiO_2 pigment for any specific application will still be inert, white, and will hide well. But, the inappropriate pigment will fall short of expectations on secondary performance characteristics such as durability, gloss, or rheology. This is in marked contrast to most color pigments where a grade inappropriate to an application is likely to fail grossly.

Matters of pigment classification are complicated by interactions among requirements:

1. Certain requirements are mutually exclusive. For example, aqueous pigment slurries are obviously suitable only for waterborne applications.
2. Some industry requirements overlap. Paper coatings resemble dry hiding paints and are served by similar products.
3. Optimal performance in one dimension can come at the expense of performance in another dimension. Flashy gloss can be attained only at the expense of pigment characteristics that promote stir-in dispersibility.
4. Premium performance can require additional process steps, increasing the cost of manufacture. Pigments for severe exposure and grades for flashy finishes are sold at a premium because they are more expensive to make.
5. Identical performance objectives can be achieved by different product designs.

Nevertheless, I have attempted classification of state-of-the-art products in terms of six performance parameters and intended applications: concentration, gloss level, exposure, optics, slurry, and dispersion. Permutations of these requirements make for 72 potential product niches for coatings applications alone. Fourteen of the niches are occupied by commercial products. They are shown in Table 3. All major manufacturers sell at least several of these products as specific grades or by equivalent sub-classifications within grades.

About two thirds of the potential product niches appear to serve no practical purpose. For example, aqueous pigment slurries are not suited for solvent-based paints, and high-PVC paint films are not made to have flashy gloss.

Obviously, the multiplicity of grades creates costs and incentives for the development of universal grades. Lately some of these attempts have been partially successful, and a few "universal" products have appeared on the market.

Conspicuously absent from this table are anatase pigments. They and the extended TiO_2 grades that used to dominate TiO_2 markets are no longer used in coatings.

OTHER WHITE PIGMENTS

In coatings, only void hiding competes with TiO_2. The classic white pigments—lithopone, zinc sulfide, zinc oxide, and white lead—are far less cost effective. White lead is also too toxic. Pigmentary zinc oxide is still being used in paint, not as a white pigment but as a mildewstat.

Extenders—colorless ground minerals and precipitated particulates—are sometimes described as pigments[31] and are advocated as supplements for true white pigments. Extenders are formulated into coatings to reduce costs by replacing expensive polymer with cheaper mineral. Below the critical pigment volume concentration, that is, in films with excess polymer, extenders do not scatter light because their refractive indices are too low. In films with excess particulates (films above their critical pigment volume concentration), extenders hide indirectly by creating pores. Only in very porous films do extenders scatter light at the particulate/air interface.

In colonial times, calcium carbonate ($CaCO_3$) was used as a white pigment. The pigment was made in situ by the reaction of atmospheric carbon dioxide with "whitewash," a brushed-on slurry of calcium hydroxide. The pigment was held together by minimal amounts of binder. Light was scattered at

[31]They do not ". . . impart black or white or a color to other materials," thus do not meet Webster's definition of a pigment.

TABLE 3—Commercial TiO_2 pigment grades.

Product Type	Intended PVC[a]	Intended Gloss	Intended Exposure	Pigment Delivery	Intended Dispersion
1	Low[b]	Flashy[c]	Indoors	Dry	High Shear[d]
2	Low[b]	Flashy[c]	Indoors	Slurry[e]	Dispersed
3	Low[b]	Flashy[c]	Outdoors	Dry	High Shear[d]
4	Low[b]	Flashy[c]	Outdoors	Slurry[e]	Dispersed
5	Low[b]	Flashy[c]	Extreme[f]	Dry	High Shear[d]
6	Low[b]	Flashy[c]	Extreme[f]	Slurry[e]	Dispersed
7	Low[b]	Discreet[g]	Extreme[f]	Dry	Low S.[h,i,j]
8	Low[b]	Discreet[g]	Extreme[f]	Slurry[e]	Dispersed
9	Low[b]	Discreet[g]	Extreme[f]	Dry	Low S.[h,i,j]
10	Low[b]	Discreet[g]	Extreme[f]	Slurry[e]	Dispersed
11	Low[b]	Discreet[g]	Extreme[f]	Dry	Low S.[h,i,j]
12	Low[b]	Discreet[g]	Extreme[f]	Slurry[e]	Dispersed
13	High[k]	Discreet[g]	Indoors[l]	Dry	Low S.[h,i,j]
14	High[k]	Discreet[g]	Indoors[l]	Slurry[e]	Dispersed

[a]Pigment volume concentration, pigments plus extenders, in the paint film.
[b]Always below the critical pigment volume concentration.
[c]Applications for which gloss is maximized at direct or indirect expense.
[d]Media mills and the like at moderate or low throughput, optimized mill base.
[e]Aqueous slurries.
[f]Including horizontal exposure to tropical and subtropical levels of UV radiation.
[g]Gloss levels from flat through semigloss to high gloss but excluding extremely high gloss.
[h]High shear dispersion is generally not required for less than extreme levels of gloss.
[i]High-speed dispersers and the like.
[j]The film qualities of low-shear dispersion are generally not satisfactory for flashy finishes.
[k]Above the critical particulate volume concentration.
[l]Coatings above the critical pigment volume concentration are usually not suited for outdoors.

the $CaCO_3$/air interface. Because the service life of the coating was minimal, whitewashing ceased when wages increased with industrialization.

Void Pigments

Air-filled voids in a paint film can either act as if they were pigment particles or enhance the effectiveness of a true pigment. Both mechanisms have been implemented in coatings.

Pigmentary and sub-pigmentary voids contribute to hiding of all dry hiding paints films, that is, films starved of binder. Somewhere above the critical pigment volume concentration voids join into an interconnected network of pores. The pores become stress concentrators that degrade the mechanical qualities of the paint film. The network conducts chemical contaminants into the paint film and to the substrate, diminishing the chemical and protective qualities of the film.

It is through the creation of pores that extenders contribute to light scattering. This scattering comes at the expense of film qualities. Problems can be avoided if the voids are sealed and spherical.

Voids of pigmentary size scatter light like particles, about as effectively as pigmentary zinc sulfide but not nearly as well as TiO_2 pigment. Unlike interconnected pores that degrade paint films, sealed spherical voids are not, per se, detrimental to mechanical and chemical film qualities.

One commerical product, Rhopaque® (Fig. 13), generates sealed, spherical air voids in paint films from plastic beads that have one concentric void. The beads are added to the paint as an aqueous dispersion of water-filled resin balloons that lose their water as the film dries. These voids are protected by the thickness of their own plastic shells from the crowding that diminishes the scattering effectiveness of conventional white pigment. Their direct light-scattering effectiveness is only 12% of scattering by the same volume of rutile. Immunity to crowding increases the effective light scattering of voids.

Another, less successful product, Pittment®, generated pigment-sized air voids in paint films by evaporation of droplets of an organic solvent emulsified in the paint.

If the voids are of sub-pigmentary size, small enough to lose their individual optical identity, they do not scatter much light but collectively decrease the refractive index of the matrix. A composite refractive index of polymer and air takes the place of the index of polymer alone. This decrease of matrix

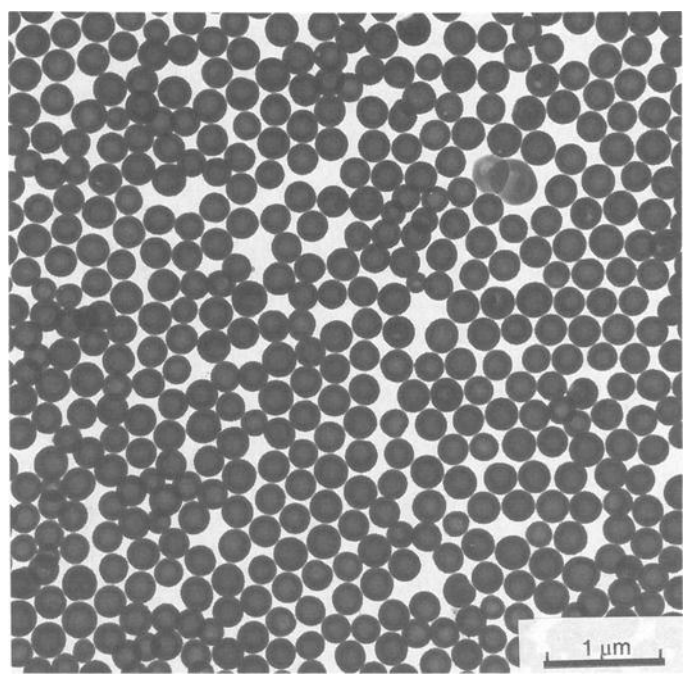


FIG. 13–Rhopaque™. From Braun, J. H., *Introduction to Pigments,* monograph in the Federation Series on Coatings Technology, Federation of Societies for Coatings Technology (United States), 1993.

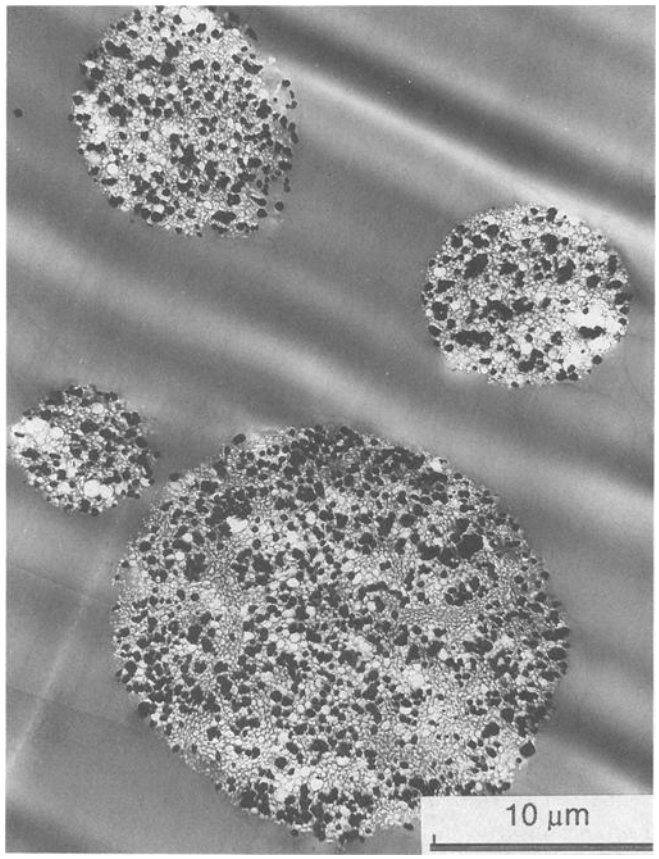


FIG. 14–Vesiculated beads. From Braun, J. H., *Introduction to Pigments,* monograph in the Federation Series on Coatings Technology, Federation of Societies for Coatings Technology (United States), 1993.

refractive index has a potent effect on the scattering of any true pigment present in the paint film.

A product composed of vesiculated and pigmented polymer beads makes use of this effect. The product, Spindrift® (Fig. 14), is suitable only for low-sheen paints because the beads act as a flatting agent. They have to be larger than TiO_2 particles because each bead has to accommodate several pigment particles plus voids and some binder.

A third approach to void hiding, the use of stretched foam, is very efficient. Hiding can be achieved without any pigment with less polymer on the substrate than by any conventional paint. But foam coatings are pressure sensitive. They are too sensitive for paint applications but are suitable for opacification of textiles, curtain fabrics in particular.

Acknowledgments

I am indebted to my former colleagues for advice, counsel, and the insights I developed during my career in DuPont's white and color pigments businesses. Special thanks go to A. Baidins and R. E. Marganski, my co-authors in a literature review of TiO_2 technology, and to D. A. Holtzen and R. C. Craft-Tulloch, who helped review and revise the manuscript.

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20

Black Pigments

by Frank R. Spinelli[1]

BLACK PIGMENTS FALL INTO three classes [*1*] (Table 1). The first two classes derive their color characteristics from the element carbon, the third class from ferrous oxide, Fe_3O_4. Class 1 blacks are carbon blacks, which are composed of 90% or more of elemental carbon. Class 2 blacks may be referred to as "carbonaceous pigments," which range from 8 to 88% elemental carbon.

CARBONACEOUS PIGMENTS (CLASS 2)

This class of blacks, perhaps the least important for paints and coatings, is composed of two main types:

Mineral Blacks

Mineral blacks are finely ground derivatives of coal and shale and are mixtures of carbon, aluminum silicates, silica, and iron oxides. They can be characterized as having poor jetness, very low tinting strength, low oil absorption, very brown undertone, and poor dispersibility. Consequently, they are rarely used in the paint industry.

Bone Blacks

Bone blacks are made by destructive distillation of solvent-extracted cattle and sheep bones and contain only from 8 to 17% carbon with the remainder mostly calcium phosphate. During the "calcination" (8 h at 800°C), the organic matter is decomposed and the resulting carbon forms a thin, porous film on the surface of the mineral network, creating a large carbon surface area per unit of weight. Consequently, they have high color and great adsorptive ability, but very weak tinting strength. Oil absorption is quite low, and aqueous dispersibility is excellent. Bone blacks are used only in specialty finishes where high color with low oil absorption is essential.

IRON OXIDE BLACKS (CLASS 3)

Naturally occurring as the mineral magnetite, these blacks are synthesized by reacting ferrous sulfate, $FeSO_4$, with alkali and then oxidizing to ferrous oxide, Fe_3O_4 (black magnetic oxide). Having the highest density as well as excellent light fastness and chemical resistance, they are used in the paint industry chiefly in metal-protective primers. It should be noted that black iron oxide, Fe_3O_4, will oxidize at high temperatures to red or brown ferric oxide, Fe_2O_3. Iron oxide blacks have very poor color and strength properties compared to carbon blacks.

CARBON BLACKS (CLASS 1)

Carbon black is the most important black pigment for paints and coatings. This unique, strictly manmade material offers great versatility in end use performance. Through variation in key properties, by careful control of manufacturing conditions, a broad range of grades is commercially available. To provide a better understanding of carbon black as a pigment in paints and coatings, the effects of carbon black property variations on its optical functioning in dispersed media are herein defined. This involves some discussion of how carbon black is formed as well as identification of its key parameters. Following is an elucidation of the mechanisms of carbon black optical function and how they are influenced by variations in each of the key parameters. Based on this knowledge, certain guidelines for selection of a grade of carbon black are enumerated. As a corollary, the subjects of achieving optimal quality dispersion and its importance to end use performance are addressed. Finally, techniques of measurement of carbon black coating's optical performance properties are outlined with reference to the appropriate ASTM tests where applicable.

Carbon Black Optical Function

General Nature of Carbon Black

1. *Principles of Formation*—The formation of carbon black requires the application of thermal energy to a hydrocarbon, usually by incomplete combustion (limited oxygen supply), which results in the rupture of C—H bonds [*2*]. This first stage is often called "cracking" (Fig. 1*A*). The reaction products are aromatic radicals and dicarbon radicals, highly reactive species, which combine to form hexagonal lattices in a planar configuration. Several "layer planes" then tend to stack to form crystallites (Fig. 1*B*). These crystallites tend to form spherical prime particles that continue to grow, forming *primary aggregates*, the characteristic units of carbon black (Fig. 2). Both prime particle and primary aggregate distributions are typically broad since a great number of layer planes and

[1]Technical consultant for Cabot Corporation, Special Blacks Division, 157 Concord Rd., Billerica, MA 01821.

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TABLE 1—Classification of black pigments.

Type	Source	Specification	Color Index and Name
Class 1: Carbon Blacks			
(a) Furnace	Oil	...	
(b) Channel	Gas	D 561	77226; pigment black 7
(c) Lamp	Oil	D 209	77226; pigment black 7
(d) Thermal	Oil and gas	...	
(e) Acetylene	Gas	...	
Class 2: Carbonaceous Pigments			
(a) Mineral	Coal	...	
(b) Bone	Bones	D 210	77267; pigment black 9
Class 3: Iron Oxides			
(a) Synthetic	Copper	D 769	77499; pigment black 6
(b) Natural	Ore	...	77499; pigment black 6

NOTE: From *ASTM Paint Testing Manual,* Black Pigments 2.8.4; 13th ed., 1972.

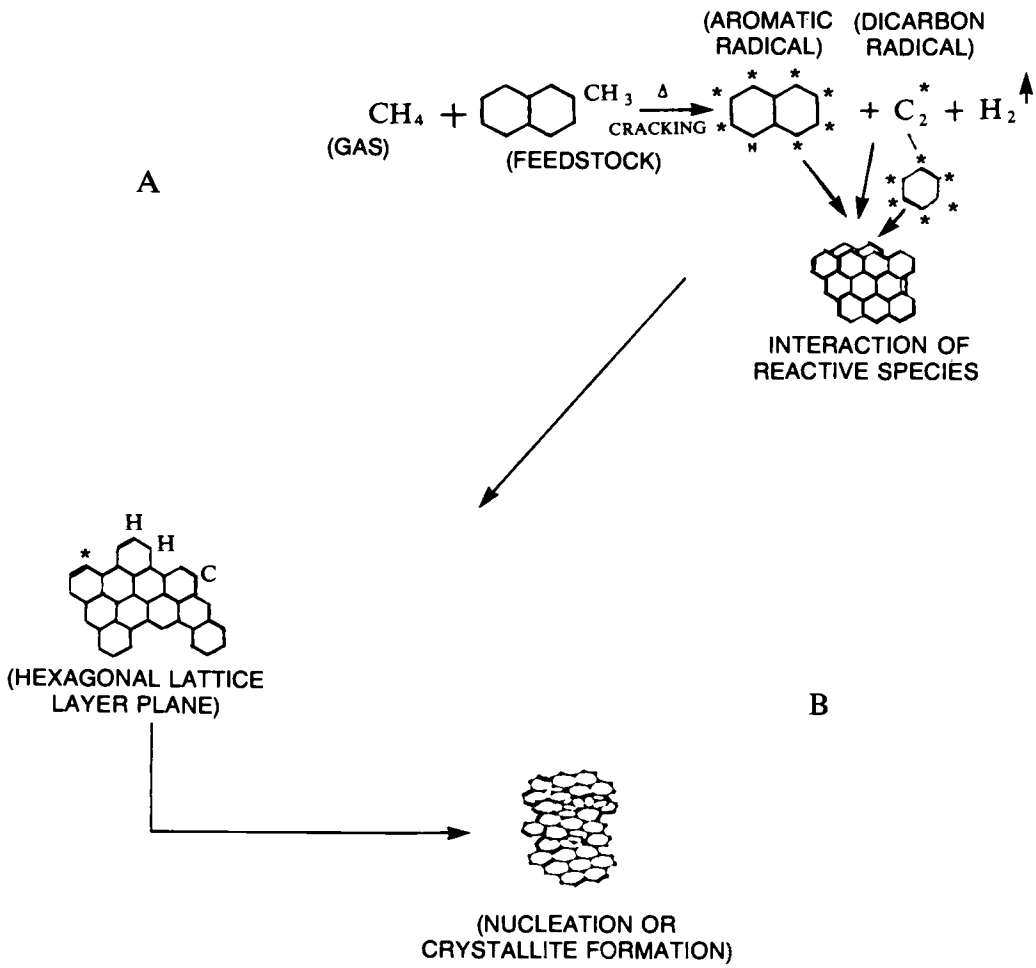

FIG. 1–Formation of carbon black. Asterisks indicate active sites.

crystallites are going through the described processes, but not in phase. Those particles and aggregates which began formation sooner would have longer growth times and would be larger. By choice of hydrocarbon feedstock and careful control of reaction conditions, the key properties of prime particle size, primary aggregate size, porosity, structure, and surface chemistry are varied to create the spectrum of commercial carbon blacks.

2. *Types/Processes* [3]—There are five types of industrial carbons which fall in the general category of carbon black. Included are lampblack, channel black, furnace black, thermal black, and acetylene black. Each of these is made by a different process and, consequently, has some unique properties (Table 2).

Lampblack Process. Oils or resins are burned in shallow pans in an enclosure with restricted air supply, and the smoke

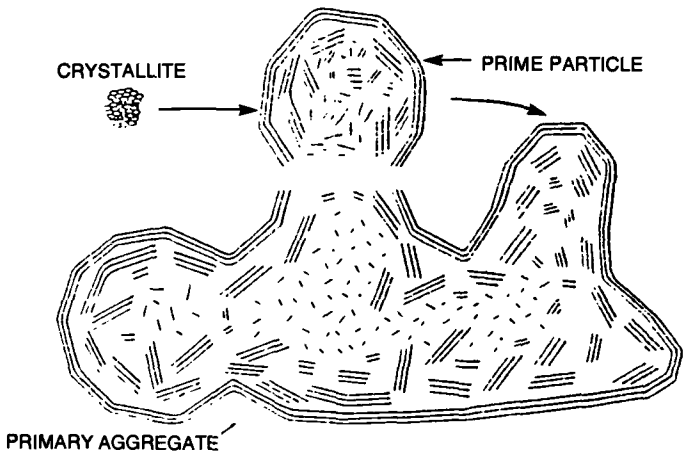

FIG. 2–Growth to particles and aggregates.

is passed through settling chambers prior to venting (Fig. 3). Carbon black deposited on the cool walls of the chambers is subsequently scraped off by motor-driven ploughs. The principal feedstocks are coal tars or petroleum residual oils. Lampblack's major usage in the coatings industry is as a tinting pigment. It exhibits excellent antiflocculation properties and an extremely blue undertone. Though lampblacks have been replaced by furnace blacks to some extent on a tinting strength basis, substantial quantities are still produced for special applications.

Channel Process. Until about 1975, this process was the leading source of carbon blacks for the coatings industry. Its demise was brought about by two principal factors: (1) the escalating cost of natural gas and (2) the increasing stringency of air pollution regulations.

The process (Fig. 4) involves partial burning of natural gas with insufficient air. Small fan-shaped flames from gas burner tips (2000 or more) are housed in sheet metal buildings or "hot houses" and are arranged so that they impinge on channel irons suspended above hoppers. Using scrapers and a reciprocating action of the channel irons, the deposited carbon is collected in the hoppers and passed through the collection system. Yields are characteristically very low, reaching a maximum of about 5% with the coarser grades. This process can produce carbon blacks of particle sizes ranging from about 30 to less than 10 nm. The resultant blacks have typically higher volatile contents (chemisorbed oxygen complexes on the surface) because of the presence of oxygen during formation. Though channel blacks have virtually disappeared from industry, a variant called roller process blacks, made from feedstocks other than natural gas, are still produced in limited quantities in Germany.

Furnace Process Blacks. These are made by partial combustion of a hydrocarbon in a closed reactor (or furnace) under well-defined conditions. The precursors of modern oil furnace blacks were the gas furnace blacks, which are no longer produced.

Oil Furnace Process. A hot flame is first created by burning gas with air inside a closed furnace, and then a liquid hydrocarbon is atomized into the hot flame zone. Furnace designs and reactor configurations vary considerably, but the principle is the same (Figs. 5a and 5b). The feedstock is usually a medium-molecular-weight aromatic oil that must be heated to 200 to 250°C to have sufficient fluidity. Yields are high (30 to 60%), air pollution is virtually nil, and it offers superior process control capability. Blacks ranging in prime particle size from 100 down to about 10 nm, with variations in structure level (degree of aggregation of prime particles), can be produced by varying furnace conditions, feedstock properties, residence times (time in hot zone), and quench distances (how far downstream the cooling sprays are introduced into the furnace).

Oil Furnace Carbon Blacks. These essentially satisfy all requirements of industrial blacks and account for 95% of all the carbon black produced today.

Thermal Cracking or Thermal Decomposition—A final category of carbon black processes uses thermal cracking or thermal decomposition of a gaseous hydrocarbon in the absence of flame. This includes thermal blacks and acetylene blacks, which are not used in the coatings industry.

Mechanisms of Interaction with Light [4]

Since coatings vehicles are usually transparent resin solutions, the function of a pigment in rendering the coating opaque and imparting a desired color is to intercept and modify incident visible light. Carbon black accomplishes this

TABLE 2—Typical analyses of carbon black grades from five different processes.

Property	Type: Furnace Symbol: HAF ASTM No.: N-330	Thermal MT N-990	Thermal FT N-880	Acetylene	Channel EPC S300	Lampblack Lb
Average particle diameter, nm	28	500	180	40	28	65
Surface area (BET), m^2/g	75	47	13	65	115	22
DBPA, mL/100 g	103	36	33	250	100	130
Tinting strength, % SRF	210	35	65	108	180	90
Benzene extract, %	0.06	0.3	0.8	0.1	0.00	0.2
pH	7.5	8.5	9.0	4.8	3.8	3.0
Volatile material, %	1.0	0.5	0.5	0.3	5	1.5
Ash, %	0.4	0.3	0.1	0.0	0.02	0.02
Composition, %						
C	97.9	99.3	99.2	99.7	95.6	98
H	0.4	0.3	0.5	0.1	0.6	0.2
S	0.6	0.01	0.01	0.02	0.20	0.8
O	0.7	0.1	0.3	0.2	3.5	0.8

NOTE: From *Encyclopedia of Chemical Technology*, Vol. 4, 3rd ed.

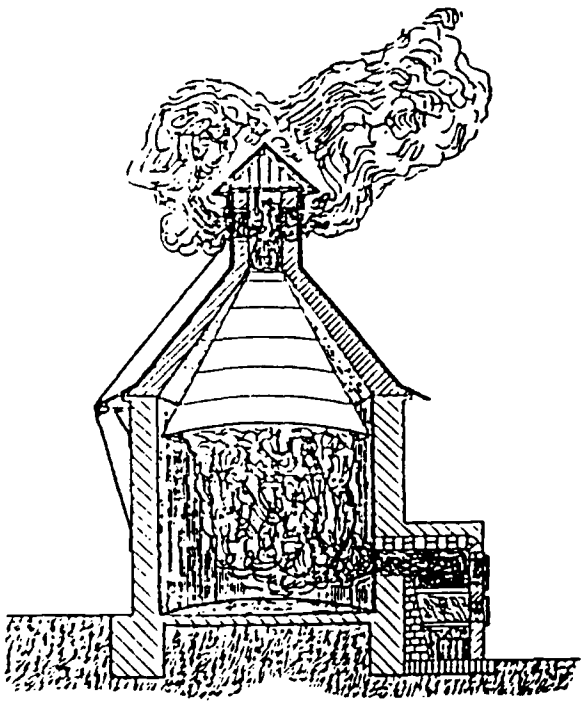

FIG. 3–Old plant for lampblack manufacture.

by means of two mechanisms: light absorption and light scattering.

1. *Light Absorption*—By nature of its quasigraphitic microstructure, carbon black strongly absorbs visible light across the spectrum. In dispersed media, because of its relatively fine particle size and high surface area, it is an extremely efficient light absorber and thus appears black. To achieve opacity, it is necessary to have a sufficient number of carbon black aggregates distributed throughout the resin matrix to intercept virtually all of the incident light (Fig. 6). This condition is often referred to as the opacity loading level and translates to about 2 to 3% carbon black by weight in most vehicle systems. Loadings of carbon black above the opacity loading level will not further enhance the color (blackness).

2. *Light Scattering* [5]—Another factor that contributes to carbon black's appearance is its relatively weak light-scattering ability. When dispersed in a vehicle, individual aggregates of carbon black are much too fine to be efficient scatterers [*6*]. Nevertheless, light scattering plays a significant part in the details of carbon black optical performance.

Carbon Black Parameters Affecting the Optical Function

General Principles

When dispersed in a transparent vehicle, the primary aggregates of carbon black are the optically functional units. Thus, the optical function is affected by variations in the two key carbon black parameters which determine aggregate size: prime particle size and structure.

As primary aggregates decrease in size, the specific surface area increases and incident light must penetrate more carbon, which results in increasing light absorption. Both absorption and scattering efficiencies (per unit weight of carbon black) increase with decreasing aggregate size (Fig. 7) down to a size equal to about one third the wavelength of the incident light, D (about 180 nm for "white light"). Further decreases in aggregate size show a leveling off of absorption efficiency and a decrease in scattering efficiency.

The size of the prime particle determines the size of the primary aggregate at a fixed level of aggregation. The level of aggregation is known in the carbon black industry as structure. It is a parameter that not only indicates the average number of prime particles composing a primary aggregate, but also the degree of anisometry, branching and chaining or shape irregularity (Fig. 8). The higher the structure, the greater the void space within and around a primary aggregate. In fact, the extent to which a carbon black absorbs oil or

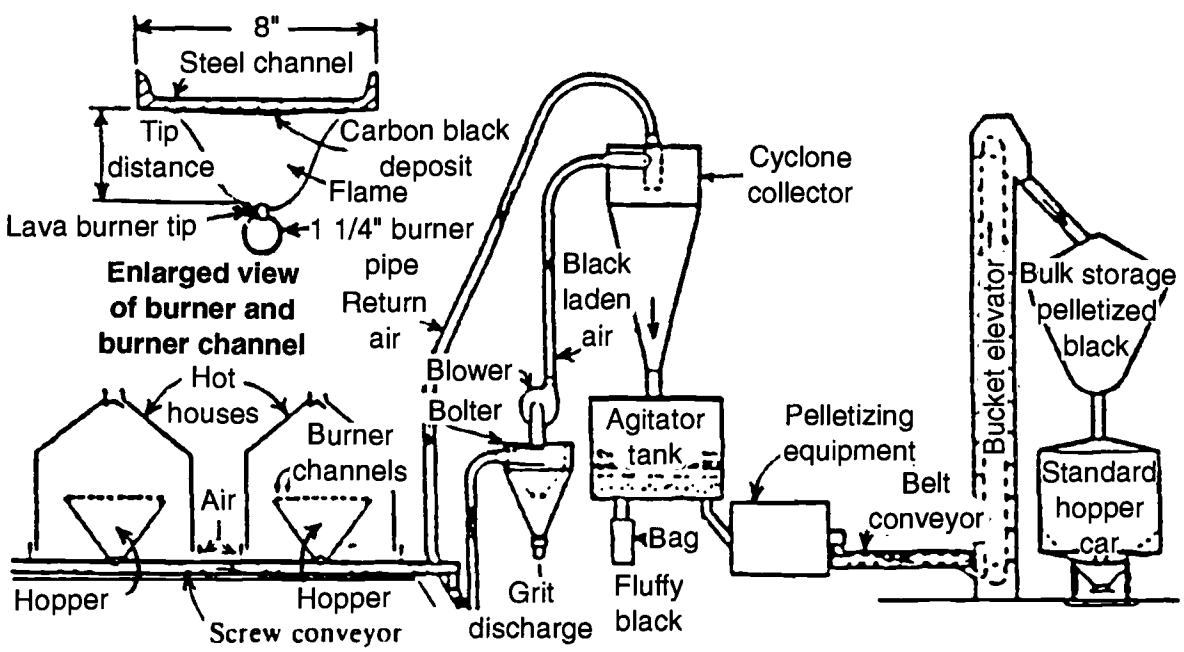

FIG. 4–Channel process for carbon black manufacture.

dibutylphthalate (DBP), which fills the void spaces, is a common industry measure of its structure.

Jetness

The industry term for degree of "blackness" is *"jetness,"* which increases with decreasing aggregate size for two reasons: (1) increasing light absorption efficiency and (2) decreasing light-scattering efficiency. As primary aggregates become smaller, incident light must penetrate more carbon, resulting in more light absorption per unit weight of black. Also, despite the individual variations of absorption and scattering efficiencies per unit weight shown in Fig. 7, the ratio [4] of absorption efficiency to scattering efficiency, *A/S*, essentially increases continuously with decreasing aggregate size. Thus, both mechanisms, absorption and scattering, are synergistic with respect to jetness, and the degree of jetness is controlled by the *A/S* ratio. The smaller the aggregate, the higher the *A/S* ratio and the jetter the black.

Structure can also be a measure of aggregate size for a given prime particle since it reflects the number of prime particles composing a primary aggregate. In this sense it is also an indicator of scattering efficiency. Low-structure blacks have smaller primary aggregates, exhibit less scattering, and have higher *A/S* ratios. High-structure blacks have larger primary aggregates, exhibit more scattering, and have lower *A/S* ratios. Given two carbon blacks of comparable prime particle size, the black of lower structure (smaller, more compact primary aggregates) will show the higher jetness because of a higher *A/S* ratio.

Tinting Strength

Carbon black's primary tinting application is to make gray colors by blending with a white pigment. Addition of a fixed amount of a number of different carbon blacks to a titanium dioxide, TiO_2, dispersion, for example, will result in various depths of gray color. The darkest gray will represent the carbon black highest in tinting strength. Since even a dark gray surface reflects a great amount of light relative to a black surface, the increment of light scattered by the carbon black is insignificant. For this reason, the controlling mechanism in tinting strength is light absorption [7]. Finer primary aggregate size, which favors increased absorption, will enhance tinting strength (Fig. 9). As the primary aggregate size is determined both by prime particle size and structure, higher tinting strength is favored by fine-particle-size, lower structure blacks. However, as shown in Fig. 7, at an aggregate size equal to one third the wavelength of incident light, the absorption efficiency, and consequently tinting strength, levels off and becomes independent of further decreases in size. This phenomenon can be seen in Fig. 9 as well.

Opacity

The extent to which a coating will cover or "hide" a substrate is a function of the nature of the pigment and its loading level. As mentioned earlier, the opacity loading level of carbon black in a coating system is usually 3% by weight or less for normal paint film thicknesses (around 1.0 mil). With much thinner films, higher loadings would be required to achieve opacity. In other words, there must be a sufficient number of primary aggregates dispersed throughout the film to prevent any significant amount of incident light from passing through.

Carbon black creates opacity through the two mechanisms cited earlier, absorption and scattering of visible light. In fact, opacity of carbon black can be considered as being directly proportional to the sum of the absorption coefficient and the scattering coefficient, $(A + S)$. This means simply that light that is either absorbed or scattered is not transmitted through the film. From this relationship, it is also possible to predict that optimum opacity, as a fixed loading, would be rendered by blacks having an aggregate size close to one third the wavelength of incident light (in short, blacks in the regular to medium color categories for white light of 180 nm, as per Fig. 7).

One convenient way to express the opacity of films is to use the parameter called *optical density*. This is a function of the percent of incident light transmitted as follows:

$$\text{Optical Density} = -\text{LOG}_{10} T_\lambda$$

where

T_λ = Transmitted light/incident light, and
λ = Wavelength of incident light.

An optical density of 1.0 would indicate a transmission of 1% (0.01), 2.0 would indicate a transmission of 0.1% (0.001), etc. Since T will vary somewhat with wavelength, it is necessary to use the subnotation to denote the wavelength of the incident light. Further, there is a logarithmic relationship with film thickness (expressed as weight of coating per unit area) for a fixed carbon black loading, i.e.

$$\text{Optical Density} = -\ln(\text{grams/m}^2)$$

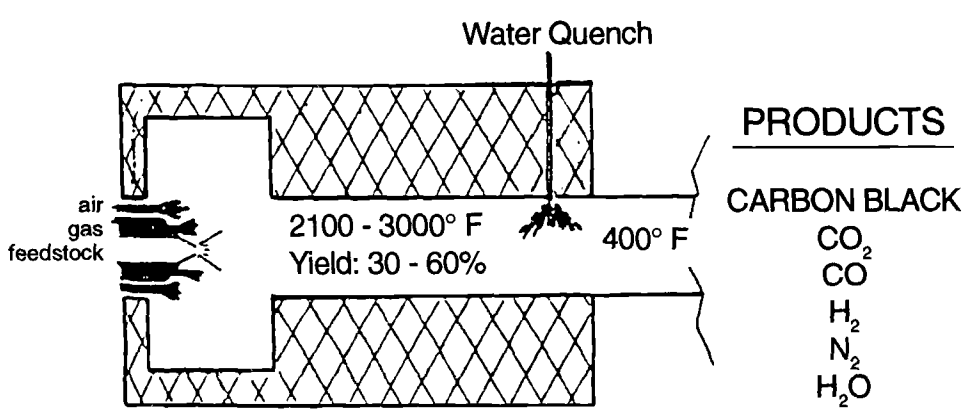

FIG. 5a–Oil furnace reactor.

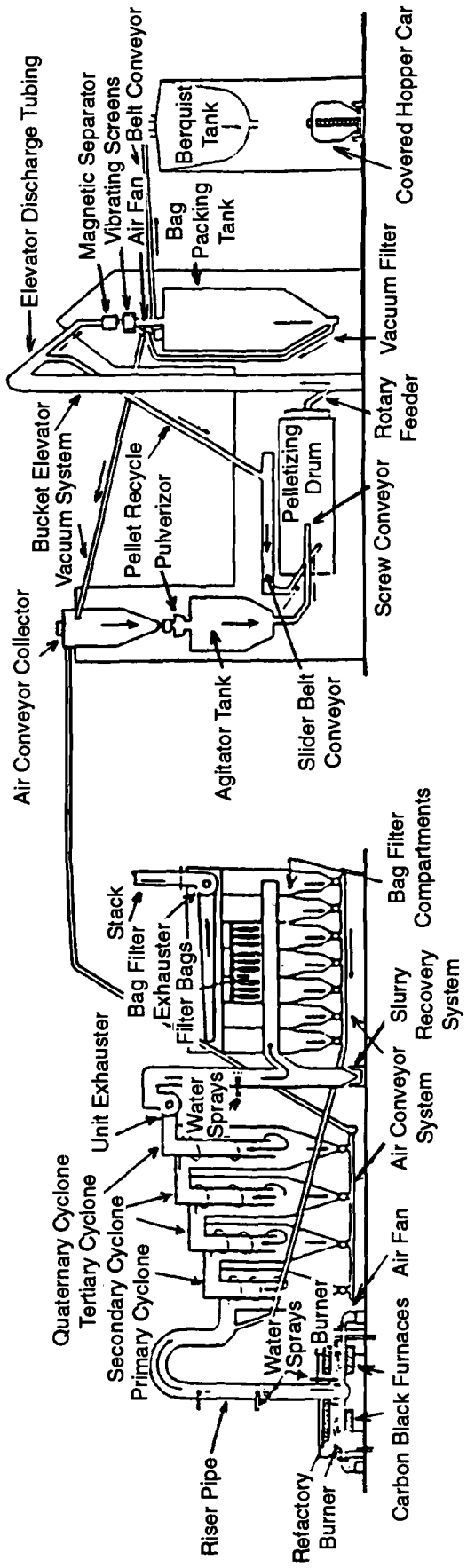

FIG. 5b–Oil furnace plant.

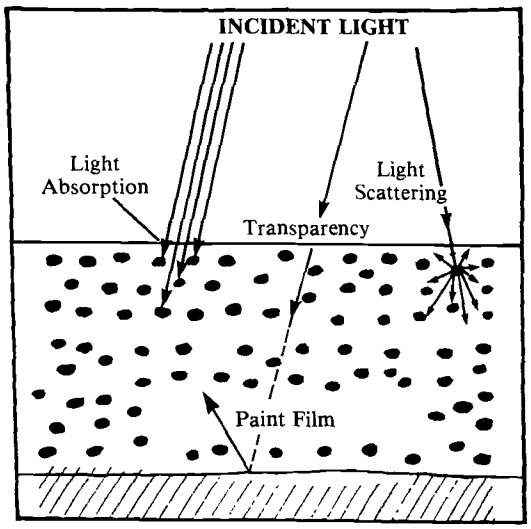

FIG. 6–OPTICAL FUNCTION OF CARBON BLACK. This diagram is an oversimplification of how carbon black functions in that primary aggregates are depicted as spherical and of roughly the same size. In reality, the aggregates are irregular in shape and occur as a distribution of sizes, which complicates the optical functioning considerably. However, the fundamental processes as shown still represent the theoretical basis for more complete treatments of the subject.

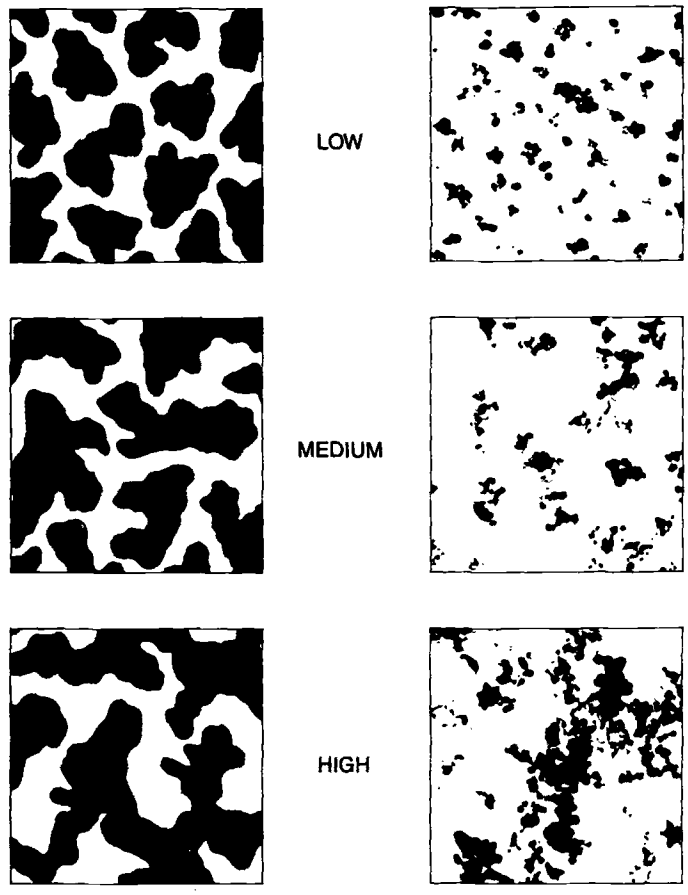

FIG. 8–Structure comparison.

Undertone

In the carbon black industry, blacks are visually characterized as having a blue or brown *undertone* or some gradation in between when dispersed in a coating system. In a black coating it is called mass tone and in a gray it is called tint tone. The phenomenon of undertone results from the fact that both scattering and absorption efficiencies of carbon black vary with wavelength [*8*]. Preferential absorption of blue light tends to make the unabsorbed light reaching the observer favor the red end of the spectrum (browner tone). The degree of preferential absorption/scattering of the blue end of the spectrum increases with decreasing aggregate size. Thus, in a gray finish, where the absorption mechanism is in

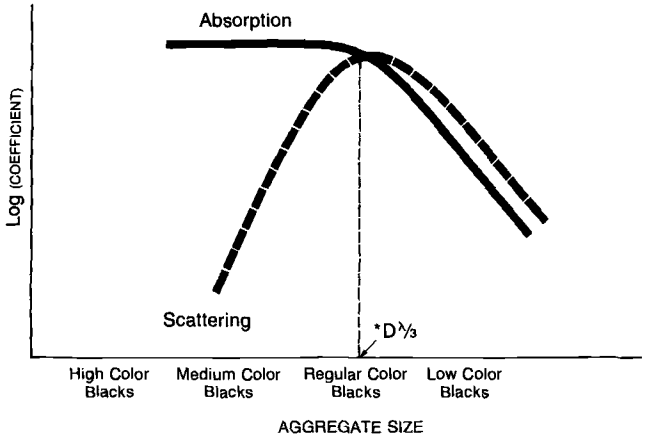

FIG. 7–CARBON BLACK OPTICS. *D λ/3 = An aggregate size equal to one third the wavelength of the incident light.

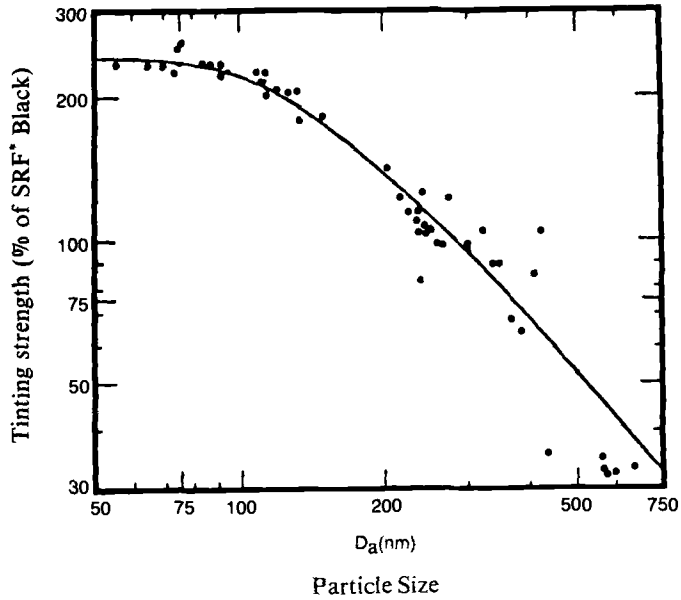

FIG. 9–Tinting strength of a range of carbon blacks.

control, the finer the aggregates the browner the tint tone. In mass tone we have the more complex situation where both preferential scattering and preferential absorption, each with a separate wavelength dependency, contribute to undertone.

Gloss

The term *gloss* is generally taken to mean the specular reflectance of a surface measured at some specific angle (for example, 60°). As with any pigment added to a transparent vehicle, the gloss of the dried film will be influenced by the loading and the properties of the carbon black. Starting with an unpigmented coating having optimal gloss in the dried film and adding a given carbon black incrementally (assuming excellent dispersions), a point will be reached where gloss begins to deteriorate until eventually the finish becomes flat. Since it is the resins in the dry film which create the smooth surface for reflection, the addition of particulate substances such as pigments or fillers in significant concentrations can only interfere with the "smoothness" of the surface.

The properties of carbon black that affect the gloss of a coating are: aggregate size, structure, and surface chemistry. Other factors being constant, the finer the aggregate size the less the effect on surface texture. The finer aggregate blacks tend to give coatings with higher gloss when properly dispersed.

Higher structure, which means more void space and therefore higher oil absorption, tends to work against gloss. This is because more vehicle is "tied up" for a given loading of black in comparing a higher structure with a low structure black. Once again we must emphasize the importance of quality of dispersion. Since higher structure blacks are somewhat easier to disperse, the effect of structure can only be properly observed in cases where optimal dispersion has been achieved.

Surface chemistry generally refers to the amount of volatile content or chemisorbed oxygen complexes on the surface (that is, hydroxylic, carboxylic, quinonic, or lactonic groups). Carbon blacks often are chemically oxidized after formation (aftertreatment) to increase volatile content. While this is usually done to improve rheological properties (for example, flow, viscosity), it normally creates improved gloss as well. The volatile content acts as a built-in dispersing agent, serving to reduce the amount of vehicle needed to completely wet the surface of the black.

The Effect of Dispersion Quality

General Principles

The influence of the key carbon black parameters on dispersibility must first be defined [9]. As the primary aggregates of carbon black become finer, dispersion becomes more difficult for two reasons: (1) higher energy needed to "wet" the higher surface areas and (2) greater attractive forces between aggregates because more particles per unit weight of carbon black means smaller interaggregate distances.

Structure plays a key role as well. Low structure blacks allow closer "packing" (higher density), which results in smaller interaggregate distances and stronger attractive forces or more difficulty in dispersion. Higher structure means more void space (lower density), which reduces interaggregate attractive forces and provides greater accessibility to vehicle penetration or greater ease of dispersion. While lower structure blacks are more difficult to disperse ultimately, they contain less occluded air (lower density) to be displaced so that they incorporate or "wet-out" more readily.

Surface chemistry can be a factor in dispersion both as volatile content or simply as adsorbed moisture. Higher volatile content, acting as a built-in dispersing agent, tends to favor easier dispersion. Adsorbed moisture, present in all carbon blacks in proportion to surface area and ambient conditions in limited amounts, has proven to be beneficial to dispersion in liquid systems.

Density and physical form of carbon black also influence dispersibility. Carbon black as produced is extremely "fluffy" and must be substantially densified (removal of occluded air by agitation), usually to over 10 lb/ft^3 for handling purposes. When the densification is done by rotary agitation in drums, either wet or dry, the result is spherical pellets, which offer ease of handling and reduced dusting. Densification packs agglomerates more closely, increasing interaggregate attraction and making dispersion more difficult. Pelletization adds the dimension of pellet hardness which must be overcome prior to actual dispersion. However, pelleted blacks "wet-out" very quickly and are thereby suitable for certain types of equipment (Table 3).

Optimal dispersion of carbon black can be defined as that condition in which all agglomerates are broken down into their constituent primary aggregates; each aggregate is separated from the others, and the surface of each is completely covered by resin. Primary aggregates are the characteristic units of carbon black and are not broken down under normal dispersion conditions. The steps involved in the dispersion process are:

1. *Incorporation (Wetting)*—This step involves the displacement of occluded air and covering the surface of agglomerates with vehicle, yielding a workable dispersion mix. Sometimes this is referred to in the coatings industry as premixing.
2. *Pellet Breakdown*—When pelleted black is used, Step 1, Incorporation, is easier since initial mixing causes little, if any, pellet fracture. Thus, at the worst, larger pellet fragments need to be "wetted" by vehicle. Pellet breakdown must then be accomplished by the application of additional energy (for example, longer mixing) after Step 1.
3. *De-Agglomeration*—This is the principal step in achieving optimal dispersion and the one that consumes most of the applied energy. Interaggregate attractive forces must be overcome to break down agglomerates into their constituent primary aggregates.

TABLE 3—Preferred form of carbon black.

	Preferred Form	
Equipment	Fluffy	Pellets
Two-roll mill		X
Three-roll mill	X	
Steel ball mill		X
Attritor	X	
Disk disperser	X	
Sand/shot mill	X	X

4. *Stabilization*—At this stage, in order to stabilize the deagglomerated aggregates, each of the aggregates must adsorb sufficient vehicle to completely deactivate its surface. This process can often be facilitated by the use of dispersing agents.

To function efficiently in an optical sense, carbon black must be optimally dispersed. The primary aggregates which characterize carbon black must be separated from one another and distributed fairly uniformly throughout the vehicle matrix to be most efficient at intercepting incident light. Choosing a grade with high surface area for high color applications, for example, must be combined with designing an effective dispersion system to ensure full color development. Mill base formulations, grade selection, physical form of carbon black (fluffy or pellets), and premixing as needed all play a part in ensuring quality dispersion. Perhaps the most important factors in mill base formulation are: (1) providing sufficient vehicle solids to accommodate the carbon black surface (Table 4) and (2) adjusting viscosity to a level suitable for the chosen dispersion equipment.

Dispersion Mechanisms

Available liquid system dispersion equipment utilizes either or both of the two main dispersion mechanisms: (1) shearing force and (2) collision of agglomerates with each other and with dispersion media particles. These mechanisms describe the manner in which energy is applied to carbon black agglomerates during the dispersion process. For example, disk disperses and three roll mills use shearing force while ball mills, sand mills, and attritors rely on collisions.

Dispersion Quality Testing

It is possible to stabilize carbon black dispersions at various levels of deagglomeration. The term *macrodispersion* is applied to very moderate levels of deagglomeration at which only the larger agglomerates are fractured. *Microdispersion*, on the other hand, refers to levels of deagglomeration approaching the ideal of single primary aggregates.

The most accurate way to measure dispersion quality is microscopically. Using X100 optical micrographs, it is possible to set up a classification system. However, it is costly and time consuming and somewhat impractical for production control. More commonly used in the coating industry is the grind gage (Hegman gage, paint club gage, etc.). These devices do not measure microdispersion. Since it is microdispersion that largely determines color performance, it is possible to have two identical mill bases, both "off-scale" on a grind gage, one of which is significantly poorer in dispersion quality. The better dispersed system would be blacker (jetter) and glossier. This leads to the most practical indirect method, that is, using color and/or gloss development, which are extremely sensitive to small variations in degree of microdispersion.

TABLE 4—Suggested vehicle solids to carbon black ratios for mill base compositions.

Type	Nitrogen Surface Area, m^2/g	Suggested Ratio, Vehicle Solids/Carbon Black
High color	230–560	3.5/1 to 4.5/1
Medium color	200–220	2.5/1 to 3.0/1
Regular color	45–140	1.5/1 to 2.0/1
Low color	25–40	1.0/1

Selecting a Grade of Carbon Black for Coloring

Black Coatings

For coloring purposes, a grade of carbon black should be selected that is as low as possible in surface area, but consistent with end use color specifications. This enables the formulator to take advantage of the greater ease of dispersion and lower cost associated with the lower surface area. The desired structure level would be high enough to give acceptable dispersibility, but not so high as to adversely affect gloss or rheology. In some cases the use of aftertreated grades will give an edge in dispersion and gloss as well as protect the rheology at higher loadings. Normally, at opacity level loadings, rheology is only a problem when more concentrated mill bases are used.

Implicit in the selection of a grade of carbon black is the choice of the fluffy or pelleted form. The choice is usually made on the basis of dispersion equipment available or on ease of incorporation or both. Listings of preferred forms for best results with each of the major pieces of equipment are helpful (Table 3). Regarding ease of incorporation, if, for example, a steel ball mill which is a very effective disperser is to be used, the edge in dispersion provided by the fluffy form is not really needed, so it is wise to consider the pelleted form which will "wet in" quickly and which creates less dust on handling.

Candidate grades must be dispersed in the specific formulation in which they are intended to be used. Keeping in mind the sensitivity of color and gloss development to dispersion quality, it is useful to evaluate jetness and gloss both at the end of the prescribed grind cycle and again after an extended cycle. This technique not only identifies which of the candidates will provide the color and gloss levels needed, but also indicates whether or not full color value from a given grade will be achieved under the prescribed dispersion conditions. The factors of carbon black cost and dispersibility must be weighed against desired color and gloss levels in making a final decision. Some commonly used oil furnace grades for the coatings industry are listed in Table 5.

Black Tinted Coatings

While selecting a black for tinting purposes involves the principles mentioned earlier under *General Natures of Carbon Black* on mass tone color, some key points need emphasis. The selection depends upon required tinting strength (see Table 5), tint tone, and relative ease of dispersion.

Tint tone (see under **Carbon Black Parameters Affecting the Optical Function** the section on *Undertone*) refers to the color undertone in tinting. If very blue undertone is needed, grades such as LCF 2 and LCF 3 are suggested. Sometimes it is necessary to sacrifice some tinting strength by going to grades with larger aggregate size in order to maximize blue tint tone (for example, going from LCF 1 to LCF 2). High-tint-strength blacks tend to give browner undertone, which is desirable in some applications.

Finally, where dispersion stability (that is, flocculation resistance) is critical, aftertreated blacks can be helpful. MFF

TABLE 5—Oil furnace black color grades for coatings.

	Grade	Jetness Index[a]	Surface Area (BET), m^2/g	Particle Size, nm	DBP Absorption, cc/100 g		Tinting Strength, %	Volatile Content, %	Density, lb/ft^3	
					Fluffy	Pellets			Fluffy	Pellets
	ASTM Test	N/A	D 3037	N/A	D 2414		D 3265	D 1620	D 1513	
High color	HCF 3	60	560	13	90	80	100	9.0	17	27
	HCF 2	64	560	13	100	90	100	9.5	16	25
	HCF 1	69	340	16	105	100	116	9.5	11	24
Medium color	MCF 4	70	230	15	70	64	120	2.0	14	29
	MCF 3	74	220	16	112	105	122	1.5	8	21
	MCF 2	73	210	17	74	68	120	1.5	15	28
	MCF 1	78	200	18	122	117	118	1.5	9	19
Flow grades	Long flow, LFF	83	138	24	60	55	112	5.0	15	32
	Medium flow, MFF	84	96	25	72	69	112	3.5	14	30
Regular color	RCF 4	83	112	24	65	60	116	1.0	15	31
	RCF 3	84	94	25	70	65	110	1.0	19	28
	RCF 2	87	80	27	85	72	104	1.0	13	29
	RCF 1	90	85	27	100	...	92	1.0	12	...
Low color grades	LCF 4	93	43	37	95	...	80	1.0	11	...
	LCF 3	95	42	41	...	121	62	1.0	...	22
	LCF 2	96	35	50	...	90	60	1.0	...	27
	LCF 1	99	25	75	72	64	58	0.5	18	33

[a]Based on Nigrometer scale values so lower numbers indicate higher jetness.
NOTE: Above data typical of commercial grades representative of the indicated categories [*11*].

(medium flow furnace) black, for example, exhibits excellent stability and high tinting strength and is often used for tinting in poorer wetting vehicles.

Measuring Appearance Properties of Carbon Black Coatings

A black coating pigmented with carbon black at the opacity level (less than 3% by weight) will probably reflect only about 1% of the light incident upon it. This presents some unique problems in trying to make absolute instrumental measurements since the sensitivity of available instruments is simply not adequate. For this reason, it has been traditional in the carbon black industry and even among end users to depend upon visual judgements of appearance properties in many cases. While no one challenges the incredible sensitivity and versatility of the human eye, it has the drawback of not being able to quantify its observations. Nevertheless, using special techniques, it is possible to obtain quantitative measurements on all appearance properties as outlined below.

Jetness

Jetness or blackness is a function of BET surface area, i.e., inversely proportional to aggregate size (Fig. 10). Traditionally, the industry assigned nigrometer "scale" values, which are a direct function of the amount of light reflected by dispersed samples (coatings, plastics, etc.). Smaller "scale" values indicated jetter carbon blacks. However, the modern approach is to measure the spectral reflectance of a black dispersion, which is made possible by the enhanced sensitivity of current instrumentation. The spectral reflectance curves can then be converted to Hunter L, a, b; or CIE coordinates [*10*] to quantitatively measure jetness and mass tone as well.

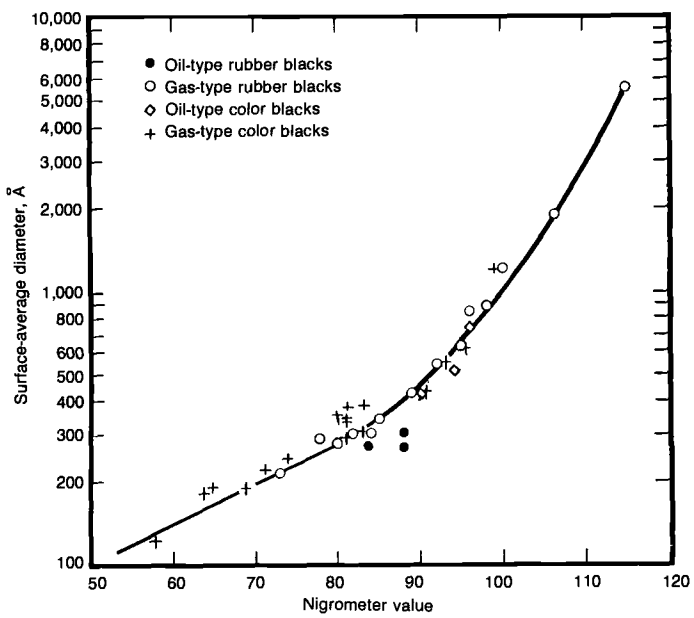

FIG. 10–Nigrometer values versus particle size for a range of carbon blacks.

Undertone

The mass tone is measured as described above in the section on jetness. This is an important tool because visual ratings of jetness are usually influenced by undertone variations among blacks being rated.

Tint tone, on the other hand, can normally be measured directly via absolute reflectance (versus a white standard) using a spectrophotometer or a colorimeter. However, common practice is to measure against a gray standard (ASTM D 3265: Test Method for Carbon Black-Tint Strength).

Tinting Strength

As illustrated in Fig. 9, tinting strength increases with decreasing particle size. The differential measurement technique, described above, is used to assign tinting strength values. The procedure, ASTM Test D 387-86, Test Method for Color and Strength of Color Pigments with a Mechanical Muller, involves dispersing carbon black together with a white pigment in a wetting oil or other suitable vehicle. The refectance of this dispersion versus a standard gray tile or gray vitreous enamel is then a measure of its tinting strength. While it was customary in the carbon black industry for many years to report tinting strength as a percent of a reference black (for example, IRB No. 4), some suppliers are now using an independent tinting strength index, allowing strength comparisons only within their own product lines.

Gloss

Clearly, this property and the manner in which it is measured is not unique for carbon black coatings. Whether the pigmentation is black or any other color, the test (for example, for 60° gloss) is the same.

SUMMARY

Individual key carbon black parameters have been viewed from the standpoint of their influence on the optical function. It is important to emphasize, however, that these parameters do not operate separately. The effect on optical functioning, and therefore on pigmentary properties, is a combined one. Each parameter when varied influences the other parameters, which are also varying. Thus the situation is dynamic and complex.

Dispersion quality and its importance in realizing the full optical potential of a given grade has also been addressed. Therefore, in the grade selection process, the physical form of carbon black as well as key parameters must be considered in light of the chosen dispersion technique.

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[*11*] Cabot Corporation, Special Blacks Division, Technical Report S136, 1988.

NOTE: References *2*, *9*, and *11* are Cabot Corporation internal publications copies of which are available from:

Cabot Corporation
Special Blacks Division
157 Concord Road
Billerica, MA 01821
Phone: 800-462-2313, Fax: (508) 670-7035
TLX: 947119

21

Colored Organic Pigments

by Peter A. Lewis[1]

DEFINITION OF A PIGMENT

Before entering into any discussion relating to pigments, it is first necessary to clearly define what is meant by a pigment as opposed to a dyestuff. In many earlier texts on color, the terms "pigment" and "dyestuff" are used almost interchangeably.

A definition of a pigment has been proposed by the Dry Color Manufacturers Association (DCMA)[2] in response to a request from the Toxic Substances Interagency Testing Committee. This definition was developed specifically to enable differentiation between a dyestuff and a pigment with the intention of forever ending the confusion surrounding these two terms. As such it is worthwhile reproducing this definition in its entirety:

> "Pigments are colored, black, white or fluorescent particulate organic and inorganic solids which usually are *insoluble* in, and essentially physically and chemically *unaffected* by, the vehicle or substrate in which they are incorporated. They alter appearance by selective absorption and/or by scattering of light.
>
> Pigments are usually *dispersed* in vehicles or substrates for application, as for instance in inks, paints, plastics or other polymeric materials. Pigments *retain* a crystal or particulate structure throughout the coloration process. As a result of the physical and chemical characteristics of pigments, pigments and dyes differ in their application; when a dye is applied, it penetrates the substrate in a *soluble* form after which it may or may not become insoluble. When a pigment is used to color or opacify a substrate, the finely divided *insoluble* solid remains throughout the coloration process."

Additionally, the terms "lake" and "toner" are encountered when dealing with pigments. American terminology, as applied to pigments, defines a toner as an organic pigment that is free of inorganic extender pigments or carriers; as such, the pigment is unadulterated and exhibits maximum tinting capacity for the pigment type. A lake, conversely, is an organic colorant that has been combined with an inorganic substrate or extender such as barium sulfate (Blanc Fixe) or alumina. In European terminology toners are considered to be water-soluble acid or basic dyestuffs that are converted to insoluble pigmentary forms by appropriate precipitation with an inorganic compound. As such, Barium Lithol red (PR 49:1) and the PTMA-based Rhodamine (PV 1) are considered toners. In the coatings industry, the term "toner" may be used to refer to a secondary color that is added to alter the hue of the paint. The term "lake" now has an accepted definition as that used in America.

A most confusing European term, the use of which should be discouraged, is "pigment dyestuff," technically an oxymoron. This term is meant to refer to insoluble organic pigments devoid of salt-forming groups, for example, Benzimidalone Orange (PO 36).

INTERNATIONAL NOMENCLATURE—THE C.I. SYSTEM

In any modern publication discussing pigments of any description, it is likely that the author will make use of the coding system as published as a joint undertaking by the Society of Dyers and Colourists (SDC) in the United Kingdom and the Association of Textile Chemists and Colorists (AATCC) in the United States.

This system is known as the "Colour Index," [*1*] and as such is a recognized trademark, hence the retention of the "u" in "colour" whenever reference is made to a "Colour Index" name or number.

The Colour Index (C.I.) identifies each pigment by giving the compound a unique "Colour Index Name" and a "Colour Index Number." This description is proving to be most valuable to persons within the coatings industry responsible for assembling data on the composition of a coatings formulation for documents such as Material Safety Data Sheets or hazard data sheets. As such the identification of a pigment by mention of its C.I. name and number unequivocally identifies the chemical composition of the pigment in a manner acceptable to most government bodies. For example, DNA Orange has the Colour Index name of Pigment Orange 5 (PO 5) and the Colour Index number of 12075.

The Colour Index Name for a pigment is abbreviated as:

PB— Pigment Blue	PBk— Pigment Black
PBr— Pigment Brown	PG— Pigment Green
PM— Pigment Metal	PO— Pigment Orange
PV— Pigment Violet	PR— Pigment Red
PW— Pigment White	PY— Pigment Yellow

[1]Coatings industry manager, Sun Chemical Corp., Colors Group, Cincinnati, OH 45232.

[2]Dry Colors Manufacturers Association, North 19th St., Arlington, VA 22209.

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CLASSIFICATION OF PIGMENTS BY CHEMISTRY

Pigments used in paints and coatings may be broadly divided into opaque or hiding whites and colored toners. All the opaque whites are inorganic compounds and as such fall outside the contents of this chapter. For the sake of clarity it should be noted that such compounds include the following:

- Lithopone (co-precipitate of barium sulfate and zinc sulfide)
- Zinc oxide
- White lead (basic lead carbonate)
- Antimony oxide
- Titanium white (mixture of titanium dioxide and blanc fixe)
- Titanium dioxide (rutile form)

The colored pigments as covered in this section are all organic in nature and as such contain a characteristic grouping or arrangement of atoms known as a "chromophore," which imparts color to the molecule. In addition, the molecule is likely to feature a number of modifying groups called "auxochromes" that alter the primary hue of the pigment in a more subtle way such as shifting a red to a more yellow shade or a blue to a more red shade while still maintaining the primary hue of red or blue rather than pushing the hue over to an orange or a violet.

Perhaps the most important of the chromophores is the azo chromophore (—N=N—). The naphthol reds, monoarylide and diarylide yellows, benzimidazolones, pyrazolones, and azo condensation pigments are all examples of organic pigments that feature the azo chromophore. Of equal importance is the phthalocyanine structure based upon the compound tetrabenzotetra-azaporphin; halogenation of this compound results in a major shift in hue from a blue to a green. Pigments are also derived from heterocyclic structures such as translinear quinacridone and carbazole dioxazine violet. Finally there are pigments that result from the vat dyestuffs and miscellaneous metal complexes.

CLASSIFICATION OF PIGMENTS BY COLOR

Reds

Metallized Azo Reds

Many reds used within the coatings industry contain the azo chromophore (—N=N—) and as such are termed "azo reds."

A further subdivision is possible into acid, monoazo metallized pigments such as Manganese Red 2B (PR 48:4) and nonmetallized azo reds such as Toluidine Red (PR 3). Typically, each of the metallized type contains an anionic grouping such as sulfonic (—SO_3H) or carboxylic acid (—COOH), which will ionize and react with a metal cation such as calcium, manganese, or barium to form an insoluble metallized azo pigment.

Conversely nonmetallized azo reds do not contain an anionic group in their structure and therefore cannot complex with a metal cation.

All azo reds contain one or more azo groups by definition and are all produced by a similar reaction sequence involving diazotization and coupling. Diazotization involves reacting the primary amine portion of the molecule with nitrous acid to yield a "diazonium salt," which is then immediately "coupled" to the other half of the molecule to yield the colored pigment.

Figure 1 illustrates the structure of a series of metallized azo reds that are of considerable commercial importance and that find some, albeit limited, use within the coatings industry. Each of these structures features a molecule based on the coupling of a naphthalene ring structure to a benzenoid structure. A brief description of the more common metallized azo reds is as follows:

Lithol Reds—Barium Lithol PR 49:1, C.I. No. 15630:1; Calcium Lithol PR 49:2, C.I. No. 15630:2.

Discovered in 1899, this pigment's major use is in the printing ink industry and finds only limited application within the coatings industry at masstone levels, that is, at a level where the tinting strength of the pigment is not diluted with a white tint base, for such reds as those used on tool boxes, fire extinguishers, and the cheaper lawn mowers where the fastness properties of the pigment are acceptable.

The pigments are bright reds with high tint strengths and good dispersion characteristics; the barium salt is lighter and

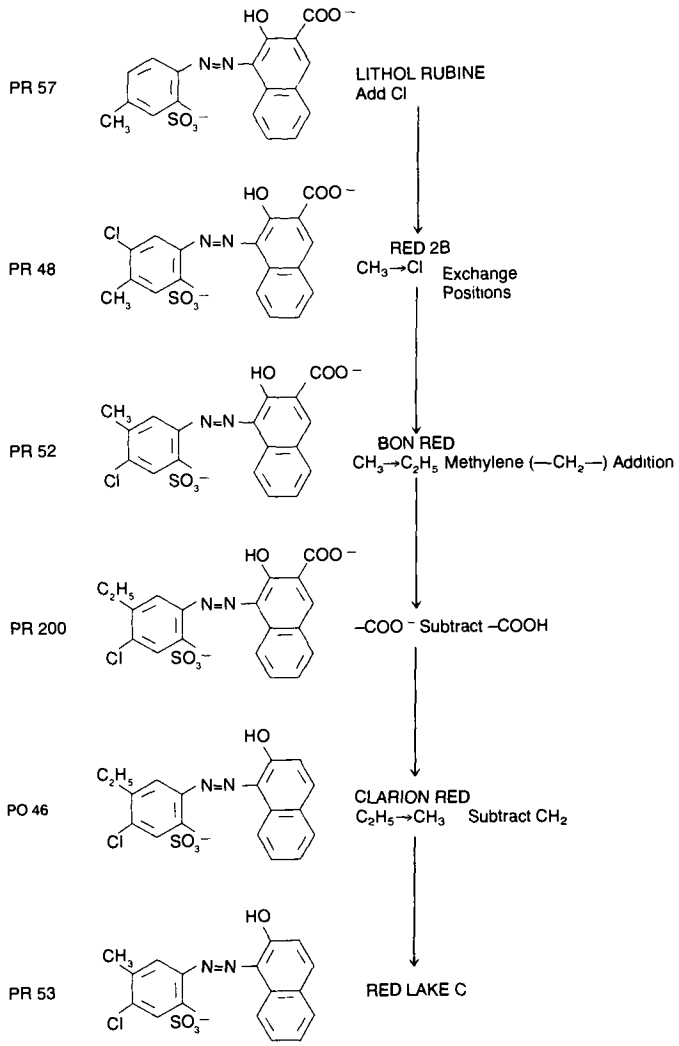


FIG. 1–Structure of metallized azo reds.

yellower in shade than the calcium salt, which may best be described as a medium red. Neither pigment can be recommended for outdoor exposure work since their exterior durability is inadequate for such situations. Additionally, they cannot be used in applications requiring pigments of high acid or alkali fastness since the Lithol Reds will hydrolyze under such conditions to give weaker, yellower shade products.

Permanent Red 2B—Barium Red 2B, PR 48:1, C.I. No. 15865:1; Calcium Red 2B, PR 48:2, C.I. No. 15865:2; Manganese Red 2B, PR 48:4, C.I. No. 15865:4.

Discovered in the 1920s, the Red 2B pigments are azo reds prepared from coupling diazotized 1-amino-3-chloro-4-methyl benzene sulfonic acid (2B acid) onto 3-hydroxy-2-naphthoic acid (BON).

A major outlet for the barium and calcium pigments is in baked industrial enamels, which do not require any appreciable outdoor fastness properties. Use in alkaline systems is again severely restricted due to the tendency of these metal salts to hydrolyze in highly alkaline environments. The barium salt is characterized by a clean, yellow hue as compared to the bluer calcium salt. The barium salt has a poorer lightfastness and weaker tinting strength but a slightly better bake stability as compared to the calcium salt.

The term "lightfastness," used throughout this section, refers to the pigments ability to withstand exposure to light, both direct and indirect, natural and artificial, without suffering any visible change in appearance. The most damaging component of light appears to lie in the ultraviolet region of the spectrum and, as such, a rapid evaluation of a pigment's likely reaction to long-term exposure to light can be assessed using exposure equipment that maximizes exposure to UV light. Many high-performance pigments are exposed under application conditions in specially maintained areas in Florida to more fully evaluate their fastness to outdoor exposure and weatherability.

The Manganese Red 2B has sufficiently improved lightfastness to allow its use in implement finishes and aerosol spray cans for touch-up paints. This salt is bluer, dirtier, and less intense as compared to the calcium salt. Extension of the Manganese pigment with any pigment such as titanium dioxide or Molybdate Orange (PR 104) to an amount greater than 15% is not recommended since its fastness properties will suffer.

Lithol Rubine Red—Calcium Lithol Rubine, PR 57:1, C.I. No. 15850:1.

Made by coupling 3-hydroxy-2-naphthoic acid (BON) onto diazotized 2-amino-5-methyl benzene sulfonic acid (4B acid), this blue shade red was discovered in 1903 and has found widespread use in the printing ink industry ever since as the process "magenta" of the four color printing process.

A clean, blue shade red with high tint strength, its major application in the coatings industry is for interior applications calling for an inexpensive red with both good solvent and heat resistance. Again the pigment must be used at near masstone levels to maximize its fastness properties.

BON Reds—Calcium BON Red, PR 52:1, C.I. No. 15860:1; Manganese BON Red, PR 52:2, C.I. No. 15860:2.

Manufactured by coupling diazotized 1-amino-4-chloro-3-methyl benzene sulfonic acid onto 3-hydroxy-2-naphthoic acid (BON), these reds first were commercialized in 1910. Characterized by outstanding cleanliness, brightness, and color purity, the manganese salt offers a very blue shade with improved lightfastness as compared to the calcium salt. As such, the manganese salt is suitable for outdoor applications and, as with the Manganese Red 2B, can be used in blends with Molybdate Orange (PR 104) to give bright, economical reds.

BON Maroon—PR 63:1, C.I. No. 15880:1.

Illustrated in Fig. 2, BON Maroon was first synthesized in 1906 by Ernst Gulbransson of Farbwerken Meister, Lucius and Bruning. The manganese salt is the only one that finds commercial significance rather than the calcium or barium variation. Its lightfastness is such that the pigment can be used at masstone levels for implement and bicycle finishes. Over 40 years ago, when specifications were not as demanding, BON Maroon actually found application in automotive finishes.

Non-Metallized Azo Reds

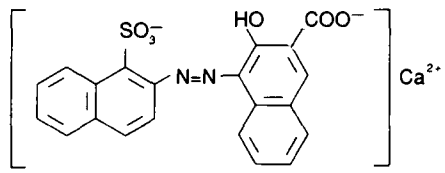
As implied by their classification, the nonmetallized azo reds do not contain a precipitating metal cation and as such offer increased stability to hydrolysis in highly acidic or alkaline environments as compared to the metallized azo reds previously covered.

Toluidine Red—PR 3, C.I. No. 12120.

This pigment, shown in Fig. 3, first synthesized in 1905, is chemically the reaction product from coupling the diazonium salt of 2-nitro-4-toluidine (MNPT) onto 2-naphthol (beta naphthol).

Various shades of Toluidine Red are available commercially described as "extra light, light, medium, dark and extra dark" as are grades offering "haze resistance" and being "easy dispersing" (ED).

Almost the entire U.S. production of Toluidine Red, an amount in excess of 0.75 million kilos, is consumed by the coatings industry. The pigment provides a bright, economical red of acceptable lightfastness when used in full shade coupled with a high degree of color intensity and good hiding power. However, the pigment is not fast to white overstriping since it will bleed through, turning the white to pink, and



2-naphthylamine-1-sulfonic acid ——→ 3-hydroxy-2-naphthoic acid (BON)

FIG. 2–Structure of BON Maroon, PR 63:1.

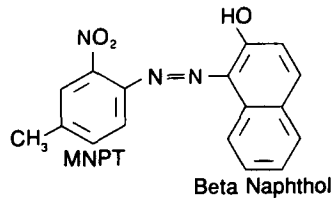


FIG. 3–Structure of Toluidine Red, PR 3.

shows a marked tendency to bleed in high Kauri-Butanol (KB) solvents.

Toluidine Red is used at masstone levels, that is, in full shade without the addition of opaque extenders such as titanium dioxide or zinc oxide, in such coatings as farm implements, lawn and garden equipment, and bulletin paints where a bright, economical red of moderate lightfastness is required to fill the user specification. Because of the pigment's poor durability in tint shades, that is as a reduction with white, it is rarely used at reduced levels.

Para Reds—Para Red, PR 1, C.I. No. 12070; Chlorinated Para Red, PR 4, C.I. No. 12085; Parachlor Red, PR 6, C.I. No. 12090.

Shown in Fig. 4, each of these three pigments is based on the coupling of a primary amine to beta naphthol. The position of the -chloro or -nitro auxochromes on the molecule controls the shade of the pigment. In fact Chlorinated Para Red differs from Parachlor Red only in the position of the -nitro and -chloro groups on the benzene ring. As such these pigments are isomers.

Use of these pigments in the coatings industry has declined rapidly due to the ever increasing and exacting demands placed upon colored finishes by the industry. All of these pigments will bleed in solvents typically used in the coatings industry and as such cannot be used in any finish that requires overstriping.

As a class of insoluble azo reds, they are characterized by intense shades of red through to a scarlet. Their good alkali resistance, lightfastness, and durability when considered as a function of their cost recommends them for use in latex paints and outdoor signs. At temperatures above 250°F (121°C), the pigments will sublime. Lightfastness of tints is significantly inferior to that of the pigments at full shade.

Naphthol Reds—Naphthol Reds are chemically defined as monoazos of 2-hydroxy naphthoic acid N-arylamides without anionic salt forming groups. Their individual properties are dependent upon the specific composition of the pigment in addition to the conditioning steps used in their manufacture. As a class they are a group of pigments that exhibit good tinctorial properties combined with moderate fastness to heat, light, and solvents. The Naphthols are extremely acid, alkali, and soap resistant pigments, properties which lead to their use in masonry paints and latex emulsions.

Naphthol Reds may be described as "medium performance" reds since they exhibit properties that fall somewhere between the Toluidine Reds and Quinacridones, with a cost that corresponds accordingly. Those Naphthol Reds of commercial significance may be briefly covered as:

Pigment Red 7, C.I. No. 12420. Used in architectural paints and some baking enamels. Offering acceptable lightfastness, even in tints, this pigment suffers from poor durability in exterior applications.

Pigment Red 22, C.I. No. 12315. A light, yellow shade Naphthol used in air drying alkyds and aqueous systems that can be satisfied with this pigments marginal lightfastness.

Pigment Red 112, C.I. No. 12370. A newer Naphthol Red that possesses a very clean, yellow hue and that finds use in both industrial and architectural coatings. The tendency of the pigment to bloom at high concentrations and its poor

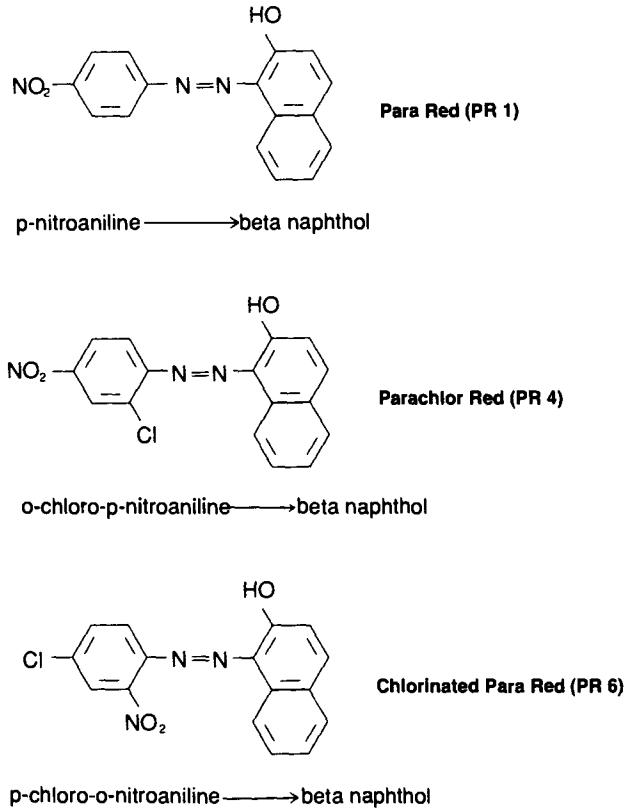


FIG. 4–Structure of the para reds.

overstriping fastness have limited its more widespread use. Lightfastness at both tint and full shade is rated good.

Pigment Orange 38, C.I. No. 12367. A very yellow shade, bright red with good solvent fastness. Can be used in baking enamels at high concentrations without showing any tendency to bloom.

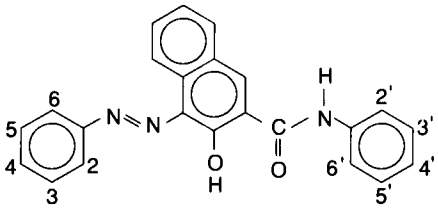
Pigment Red 5, C.I. No. 12490. Showing only marginal fastness to heat and solvents this pigment, nevertheless, finds application in implement coatings. The opaque grade of this pigment can be combined with iron oxide to give an economical red with high hiding.

Pigment Red 146, C.I. No. 12485. A very blue shade red that finds its major use in interior architectural applications. Its poor exterior durability makes the pigment unsuitable for outdoor finishes.

Pigment Red 170, C.I. No. 12475. Increasingly important as a medium performance, moderately priced red, this pigment is available as both a transparent and an opacified grade. Manufacturing techniques are used to produce the pigment in two crystal phases, each exhibiting a unique hue. The opaque grade finds use in farm tractor and implement finishes. Its use with iron oxides allows a practical approach to formulating reds with acceptable lightfastness, hiding, and economics.

Pigment Red 187, C.I. No. 12486. A transparent pigment with excellent heat fastness, moderate durability, and good bleed resistance. Its uses extend to bicycle coatings, coil, and, powder coatings.

Pigment Red 188, C.I. No. 12467. A yellow, clean shade red with acceptable durability at all depths of shade. It is fast to



Colour Index Name	Colour Index Number	Substituents 2	4	5	2′	4′	5′
PR 2	12310	Cl	H	Cl	H	H	H
PR 7	12420	CH_3	Cl	H	CH_3	Cl	H
PR 9	12460	Cl	H	Cl	OCH_3	H	H
PR 10	12440	Cl	H	Cl	H	CH_3	H
PR 14	12380	NO_2	Cl	H	CH_3	H	H
PR 17	12390	CH_3	H	NO_2	CH_3	H	H
PR 22	12315	CH_3	H	NO_2	H	H	H
PR 23	12355	OCH_3	H	NO_2	H	H	NO_2
PR 112	12370	Cl	Cl	Cl	CH_3	H	H

FIG. 5–Generic structure and key to the naphthol reds.

overstriping at temperatures below 160°C and therefore finds use in the higher quality industrial finishes. Figure 5 illustrates the generic structure of the naphthol molecule and gives the chemistry of several of the types discussed above.

High-Performance Reds

These types of pigments may be broadly defined as products that will meet the exacting demands of the automotive industry with respect particularly to the outdoor exposure requirements demanded by exposure in Florida and Arizona for as little as two and as long as five years.

The high-performance reds considered fall into four basic classes: quinacridone reds and violets, vat dyestuff based reds such as perylenes, benzimidazolone reds, and disazo condensation reds.

Quinacridone Reds—These are heterocyclic in nature since their structure comprises a fused ring in which the ring atoms are dissimilar, being a combination of carbon and nitrogen rather than only carbon as we have seen in the previous pigments discussed, as shown in Fig. 6. Addition of differing auxochromic groups such as methyl (—CH_3) and chlorine (—Cl) gives Pigment Red 122 and Pigment Red 202, respectively, both described as magentas.

The theory behind the superior durability of pigments with the quinacridone structure is that considerable hydrogen bonding occurs between molecules through the carbonyl (=C=O) and imino (=N—H) ring atoms.

As a group of pigments the quinacridones find their primary uses in automotive, industrial, and exterior finishes. A minor use is in the preparation of quality furniture stains and finishes. The pigments combine excellent tinctorial properties with outstanding durability, solvent fastness, lightfastness, heat fastness, and chemical resistance. Table 1 lists those shades currently commercially available.

Vat Reds—Vat Red pigments based upon anthraquinone include such structures as Anthraquinone Red (PR 177), Perinone Red (PR 194), Brominated Pyranthrone Red (PR 216), and Pyranthrone Red (PR 226) as shown in Fig. 7.

The term "vat pigments" originates from the fact that this class of pigments is related to the vat dyestuffs used originally

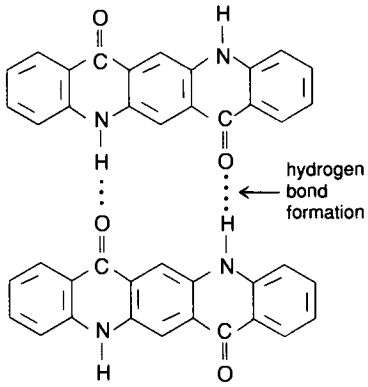


FIG. 6–Trans linear quinacridone showing proposed hydrogen bonding mechanism.

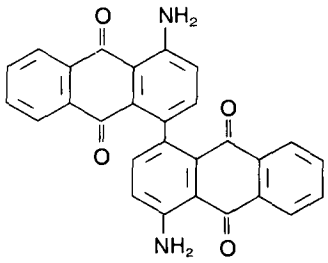
in the dyeing of cotton. Only their high cost limits the more widespread use of these pigments throughout the coatings industry.

Anthraquinone Red, PR 177, C.I. No. 65300. A medium shade red with excellent all round fastness properties. Again finds major use in the automotive industry for the production of clean, bright red coatings.

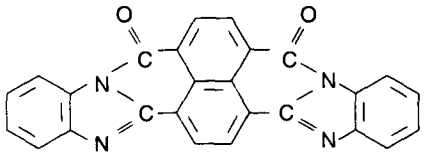
Brominated Pyranthrone Red, PR 216, C.I. No. 59710. A yellow shade red that also can be classed as an automotive grade pigment because of its excellent fastness properties. Neither light nor dark shades will suffer on prolonged expo-

TABLE 1—Types of quinacridone.

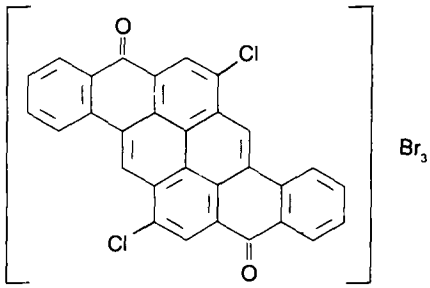
Colour Index Name	Hue	Comments
PO 49	Gold	Quinacridone quinone
PR 122	Magenta	2,9-dimethyl
PR 192	Red-yellow	Mono methyl
PR 202	Magenta	2,9-dichloro
PR 206	Maroon	Solid solution
PR 207	Scarlet	4,11-dichloro
PR 209	Red-yellow	3,10-dichloro
PV 19	Violet-blue	Beta crystal
PV 19	Red-yellow	Gamma crystal
PV 42	Maroon	Solid solution



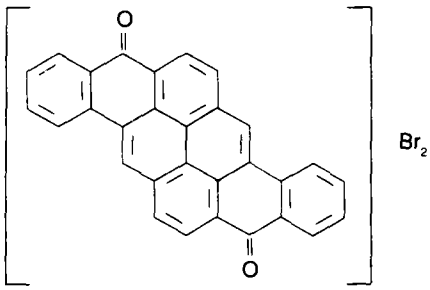
Anthraquinone Red (PR 177)



Perinone Red (PR 194)



Brominated Pyranthrone Red (PR 216)



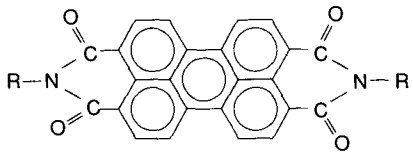
Pyranthrone Red (PR 226)

FIG. 7–Structure of typical vat reds.

sure in Florida. Transparency is generally not adequate for this pigment to be used in metallic or mica finishes.

Perylene Reds—These pigments provide pure, transparent shades and novel styling effects when used in metallic aluminum and mica finishes. The perylenes offer improved flow characteristics when used in high-solids formulations. Perylenes may also be described as vat pigments and in fact are the only class of Vat pigments that were developed specifically for the pigment marketplace rather than as dyestuffs.

Almost all of the perylenes have a structure as shown by the generic formula given as Fig. 8, that is, they are based upon



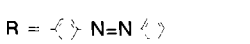
R = $-C_6H_3OC_2H_5$	PR 123	Vermillion
R = $-C_6H_3(CH_3)_2$	PR 149	Scarlet
R = $-CH_3$	PR 179	Maroon
R = $-C_6H_5OCH_3$	PR 190	Red
R = $-H$	PBr 26	Bordeaux
R = $-C_6H_5Cl$	PR 189	Yellow Shade Red
R = 	PR 178	Red

FIG. 8–Structure of typical perylene.

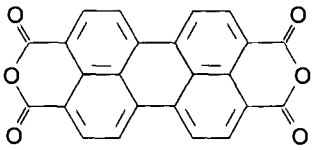
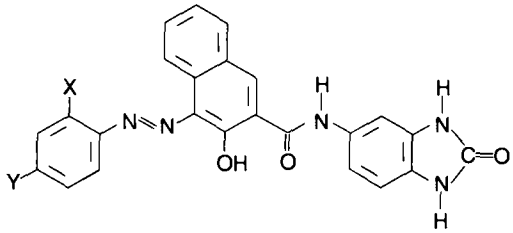


FIG. 9–Structure of Pigment Red 224.

N,N′-substituted perylene-3,4,9,10-tetracarboxylic di-imide. An exception of note is Pigment Red 224, Fig. 9, which is derived from the perylene tetracarboxylic dianhydride.

Benzimidazolone Based Reds—This subdivision of reds includes such pigments as Pigment Reds 171, 175, 176, 185, and 208. Benzimidazolone-based reds are azo reds that contain the benzimidazolone structure as part of their makeup. The reds all possess the generic structure based upon a central naphthol molecule as illustrated in Fig. 10. Such structures exhibit a significantly high molecular weight that greatly influences the pigments fastness properties.

Benzimidazolone reds are used primarily in the coloring of plastics because of their outstanding heat stability, although some uses are found within the coatings marketplace. They show excellent fastness to light at all depths of shade, good weatherability, and excellent fastness to overspraying at elevated temperatures. They all find use in coil coatings, powder coatings, camouflage paints, automotive refinish, and farm



Colour Index Name	X	Y
PR 171	OCH_3	NO_2
PR 175	$COOCH_3$	H
PR 176	OCH_3	$CONHC_6H_5$
PR 185	OCH_3	SO_2NHCH_3
PR 208	$COOC_4H_9$	H

FIG. 10–Structure of the benzimidazolone reds.

implements where cheaper, less stable pigments would be inadequate.

Pigment Red 175 is a highly transparent red with good lightfastness that finds application in automotive base coat/clear coat systems since it is not sufficiently durable for top coat systems. Pigment Red 171 is also a transparent pigment but with a maroon shade that finds use in industrial systems. Pigment Reds 176, 185, and 208 find considerable use in quality printing ink applications but currently no use in the coatings industry.

Disazo Condensation Reds—These types of pigments have been available commercially in Europe since 1957 and in the United States since 1960. Their outstanding fastness properties have resulted in their use in high-quality industrial finishes.

Figure 11 illustrates three typical structures of the disazo condensation reds. The figure merely serves to show the size and variation of the structures of pigments within this class; no Colour Index names are available at present.

Pigment Red 242, Fig. 12, is a bright yellow shade disazo condensation pigment with excellent fastness properties that is finding increased use in high-quality industrial finishes and as a lead replacement pigment for those high-quality coatings that now must be formulated lead free.

Pigment Red 214, Fig. 13, is another example of a disazo condensation red with properties similar to Pigment Red 242.

Thioindigoid Reds—The thioindigoid chromophore serves as a nucleus for a wide range of red to violet pigments including such as Pigment Reds 86, 87, 88, 181, and 198, Fig. 14. These pigments are all noted for their brightness of shade and generally good fastness properties, resulting in their use in the coatings industry with Pigment Red 88 being the largest volume used followed by Pigment Red 198. Pigment Red 88 is widely used in automotive finishes, but the bleed resistance of Pigment Red 198 limits its use. The commercially availability of these pigments has suffered in recent years with many products having been withdrawn from the marketplace by the almost exclusive supplier, Bayer.

Novel High-Performance Reds

In recent years several novel organic reds have been commercialized and targeted directly at the requirements of the coatings marketplace.

Pigment Red 257, Fig. 15, is a nickel complex with a red-violet masstone and a magenta undertone that exhibits fastness properties similar to that of quinacridone. Pigment Red 257 is particularly useful in the formulation of high-quality industrial and automotive coatings. The pigment also exhibits excellent rheological properties in highly pigmented systems.

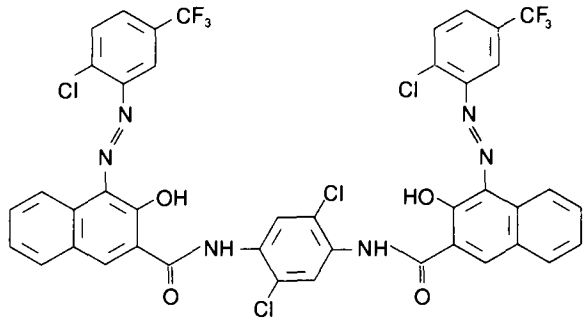


FIG. 12–Structure of Pigment Red 242.

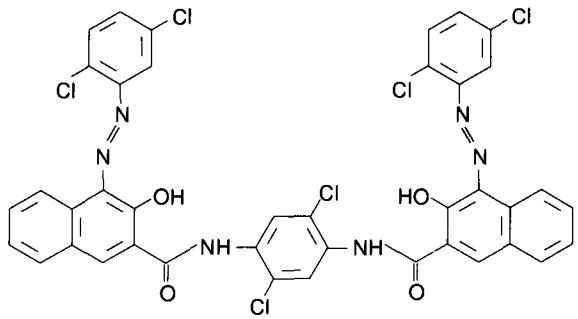


FIG. 13–Structure of Pigment Red 214.

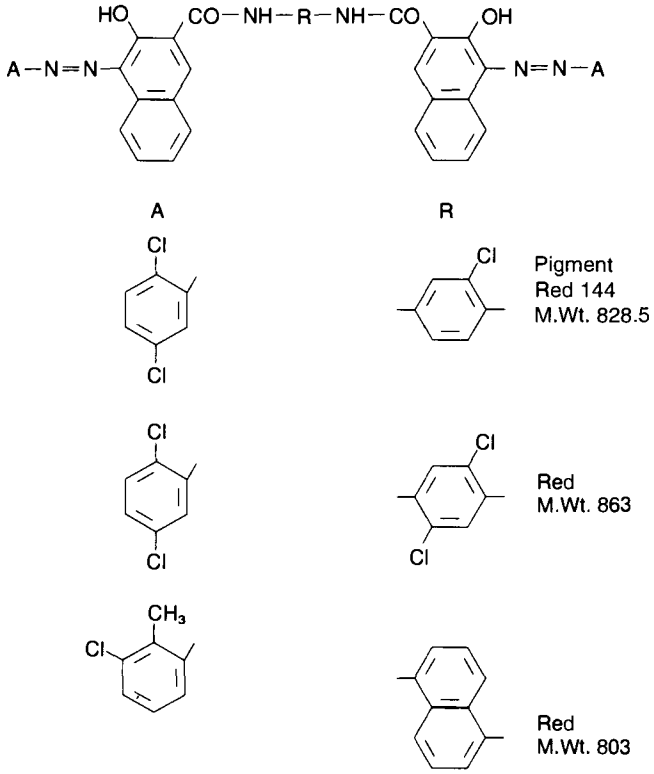
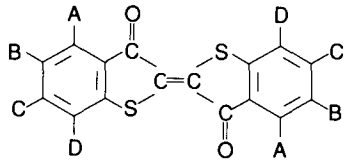


FIG. 11–Structure of the disazo condensation reds.



A	B	C	D	
–CH_3	–H	–Br	–H	PR 86
–H	–H	–H	–Cl	PR 87
–Cl	–H	–H	–Cl	PR 88
–CH_3	–H	–Cl	–H	PR 181
–Cl	–H	–H	–CH_3	PR 198
–H	–Cl	–H	–CH_3	PV 36
–CH_3	–Cl	–H	–CH_3	PV 38

FIG. 14–Structure and key thioindigoid reds.

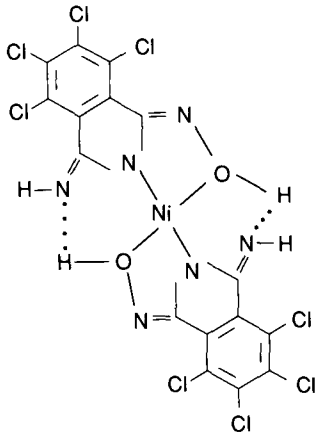


FIG. 15–Structure of Pigment Red 257.

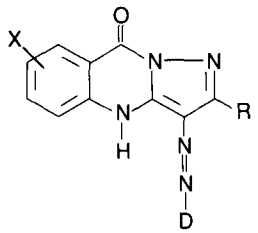


FIG. 16–Generic structure of pyrazoloquinazolone (basis of Pigment Red 251 and 252).

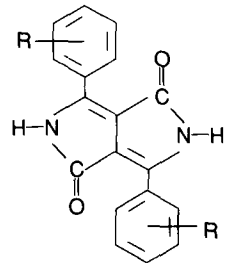


FIG. 17–Generic structure of pyrrolo-pyrrole.

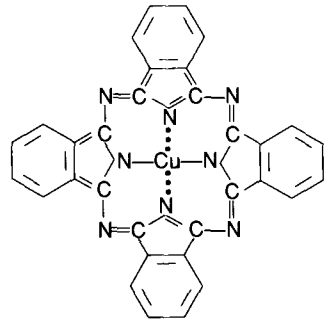


FIG. 18–Copper phthalocyanine, PB 15.

Pigment Reds 251 and 252 are both based on the pyrazoloquinazolone structure as shown in Fig. 16. These pigments are monoazo compounds derived from pyrazolo(5,1-b)quinazolones as the coupling component and substituted anilines or polycyclic amines as diazo component. Each pigment exhibits excellent brightness of hue at full shades, good gloss retention, and high scattering power combined with good light and weather fastness. As such, they are finding increased use in industrial and automotive coatings.

Recently a series of novel reds based upon the pyrrolo-pyrrole structure, Fig. 17, have been marketed into the automotive coatings industry. The first pigment marketed is a bright red with excellent color intensity that will find use alongside quinacridones and perylenes in automotive formulations.

Blues

Copper Phthalocyanine Blue

The most important and most widely used blue throughout all applications of the coatings consuming industry is copper phthalocyanine blue, Pigment Blue 15, Fig. 18.

First described in 1928 by chemists working for the Scottish Dye Works (now part of I.C.I.), this pigment has steadily increased in importance to become a product with worldwide significance. The only metal derivative of significant commercial use is that of copper, derivatives of other metals having been shown by research to have less desirable shade or fastness characteristics. Metal-free phthalocyanine, Pigment Blue 16, once found an outlet as a green shade blue, but its inferior heat stability and its poorer chemical fastness, coupled with a price almost three times that of the copper containing salt, has resulted in a rapid decline in its consumption for all but very special applications.

Copper phthalocyanine is commercially available in two crystal forms, the alpha and the beta form. The alpha crystal is described as Pigment Blue 15, 15:1 and 15:2 and is a clean, bright red shade blue. The beta crystal is described as Pigment Blue 15:3 and 15:4 and is a clean green or peacock shade.

The beta form is the most stable crystal form and readily resists recrystallization. The alpha form, conversely, is the least stable or meta form, which readily converts to the more stable, green shade, beta crystal. As such the crystal requires special proprietary treatments to produce a red shade product that is stable to both crystallization and flocculation.

Copper phthalocyanine gives excellent performance in most coatings applications but there is considerable variation between both the chemical and crystal types available. The coatings formulator should bear this in mind when choosing a grade for a specific application. Use of any of the unstabilized grades in strong solvents or in systems that experience heat during dispersion or application will result in a shift in shade to the greener side and a loss of strength as recrystallization takes place within the unstabilized crystal.

Pigment Blue 15 (C.I. No. 74160) is a red shade, alpha crystal. It is the least stable of the family and as such is referred to as crystallizing red shade (CRS) blue.

Pigment Blue 15:1 is a modified alpha crystal also having a red shade but with modifications to stabilize the structure against phase transformation to the beta crystal. Most commonly the molecule is chlorinated to the extent of one molecule of chlorine per molecule of copper phthalocyanine to give "monochlor" blue (C.I. No. 74250).

Pigment Blue 15:2, described as "non-crystallizing non-flocculating" (NCNF), red shade blue, is an alpha crystal that is stabilized against both flocculation and recrystallization using additive technology. Such additives are introduced during the manufacturing or blending operation and are essentially derivatives of copper phthalocyanine that confer stability by a steric hindrance mechanism.

Pigment Blue 15:3 represents the most stable crystal, green shade, beta copper phthalocyanine. Pigment Blue 15:4 is descriptive of a beta blue that has been modified with phthalocyanine-based derivatives to confer flocculation resistance to the crystal such that it can safely be used in strong solvent systems.

Other specialized, more expensive crystal modifications also exist such as P.B. 15:5, a red shade, gamma crystal and P.B. 15:6, a very red shade, epsilon crystal.

Copper phthalocyanine is a pigment that offers brightness, cleanliness, strength, and economy with all round excellent fastness properties. The only drawback to this pigment is its tendency to change to a coarse, crystalline nonpigmentary form when used in strong solvent systems if the crystal has not been adequately stabilized and has a tendency to flocculate from white pigments such as titanium dioxide when used to tint such paint and lacquer systems. Another negative is the fact that copper phthalocyanine blues exhibit the phenomenon of bronzing when applied at masstone levels, deep tints, and in metallic systems.

Miscellaneous Blues

Indanthrone Blue—Pigment Blue 60, C.I. Number 69800.

Belonging to the class of pigments described as "vat pigments," indanthrone blue is a very red shade, nonbronzing, flocculation-resistant pigment with outstanding fastness properties. This pigment is used in paint systems requiring only small amounts of an intense red shade blue as a shading pigment at low levels where the expense of using indanthrone blue is justified.

Carbazole Violet—Pigment Violet 23, C.I. Number 51319.

A complex polynuclear or heterocyclic, intense red shade blue pigment that possesses excellent fastness properties. Only the pigment's relatively high cost and hard nature limit its more widespread use. The pigment is used at very low levels to produce "brighter whites" by imparting a bluer hue to the undertone of the white.

Yellows

Monoarylide Yellows

Azo pigments whose manufacture is based upon the diazotization and coupling sequence as mentioned when dealing with azo reds. The structures of the major monoarylide yellows are represented in Fig. 19.

Hansa Yellow G—Pigment Yellow 1, C.I. Number 11680.

A bright yellow pigment, made by coupling diazotized 2-nitro-4-methyl aniline onto acetoacetanilide, that has a major use in trade sales, emulsion, and masonry paints. Its major disadvantages are its poor bleed resistance in most popular solvents, poor lightfastness in tint shades, and very inferior bake resistance due to its tendency to sublime.

Hansa Yellow 10G—Pigment Yellow 3, C.I. Number 11710.

A very green shade yellow made by coupling the diazo of 4-chloro-3-nitro aniline onto 2-chloro acetanilide. Greener in shade than Pigment Yellow 1, this pigment is used in the same types of applications and suffers from the same defi-

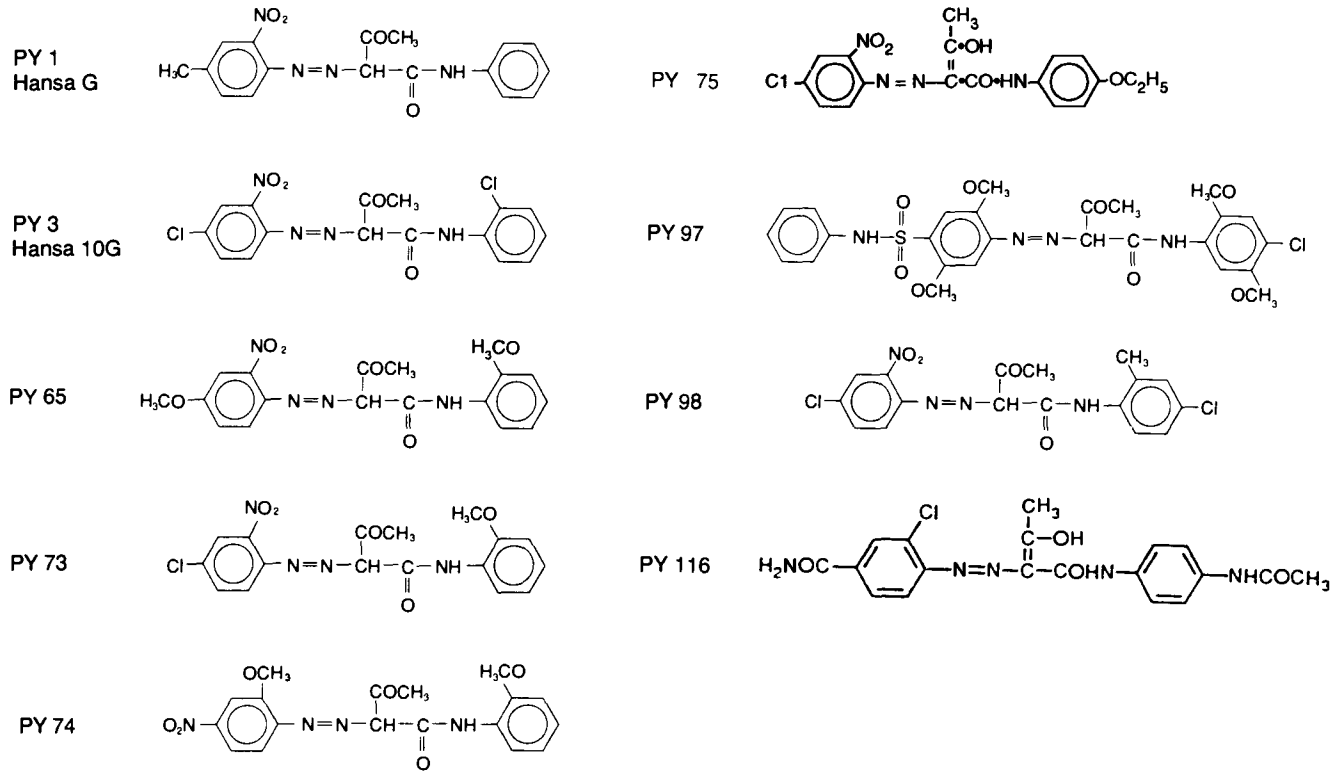


FIG. 19–Structures of the major monoarylide yellows.

ciencies as Pigment Yellow 1 with the exception that Pigment Yellow 3 is suitable for use in exterior applications at high tint levels.

Miscellaneous Monoarylide Yellows—Pigment Yellow 65, C.I. Number 11740: A newer monoarylide pigment produced by coupling diazo 2-nitro-methoxy aniline onto 2-acetacetanisidine. Offering a redder shade than the previous two yellows discussed. Pigment Yellow 65 is used in trade sales, latex, and masonry paints. A more recent application is for road traffic marking paints that are specified as being lead free. The bleed resistance and baking stability are little improved over Pigment Yellows 1 and 3.

Pigment Yellow 73, C.I. Number 11738: Prepared by coupling diazo 3-chlor-2-nitro aniline onto 2-acetoacetanisidine, this is a pigment with a shade close to that of Pigment Yellow 1 that finds use in similar applications. Not considered durable enough for exterior applications, Pigment Yellow 73 nevertheless plays an important role in interior, intermix systems due to its stability against recrystallization in the presence of glycols and wetting agents used in latex systems.

Pigment Yellow 74, C.I. Number 11741: A product from the coupling of diazo 4-nitro-2-anisidine onto 2-acetoacetanisidide which offers the user a pigment suitable for outdoor applications that is considerably stronger and somewhat greener than Pigment Yellow 1. Major outlets, as with all the monoarylide yellows, are in latex, trade sales, and masonry paints. Additionally a specially opacified grade is available that is optimized for its exterior durability although of lower tint strength than the normal more transparent grade.

Pigment Yellow 73 and the opaque grades of Pigment Yellow 74 show the least tendency to crystallize in organic solvent containing systems.

Pigment Yellow 75, C.I. Number 11770: A pigment produced by the coupling of 4-chloro-2-nitroaniline onto acetoacetophenetidide. A red shade yellow that has only recently found considerable application in the coatings industry as a replacement for lead containing medium chrome yellow as used in road traffic marking paints. One of the few diarylide yellows that has been found acceptable from the point of view of economy and durability, being able to withstand nine months exposure on a 100 000 vehicle a day highway. A point worthy of note is that this pigment appears to be inherently "easy dispersing" since the economics of the traffic paint industry demand that any pigment used to replace lead chromes must be dispersed into water or solvent systems with little more than a "Cowles" type disperser.

Pigment Yellow 97, C.I. Number 11767: A yellow derived from the coupling of diazo 4-amino-2,5-dimethoxybenzene sulphoanilide to 4-chloro-2,5-dimethoxy acetoacetanilide. Surpassing the Hansa yellows in solvent bleed and lightfastness, especially in reduced shades, this newer yellow is finding use in high-quality decorating paints.

Pigment Yellow 98, C.I. Number 11727: Similar in shade to Pigment Yellow 3, but considerably stronger and more heat stable, this pigment has only met with limited commercial success in trade sales, masonry and decorative paints. Manufacture by coupling diazo 4-chloro-2-nitro aniline onto 4-chloro-2-methyl acetoacetanilide.

Pigment Yellow 116, C.I. Number 11790: A product from the coupling of diazo 2-chloro-5-carbamoyl aniline onto 4-acetylamino acetoacetanilide, this pigment is similar in shade to light chrome yellow (PY 34) and shows improved light, heat, and solvent fastness as compared to the other monoarylide yellows. As may be expected from its shade, this pigments major use is in lead-free coatings.

Diarylide Yellows

The structures of this commercially important range of organic yellows are shown in Fig. 20. This figure clearly shows the similarity between each of these pigments, which are principally a backbone structure centered on 3,3′-dichlorobenzidine with modifications to the shade and properties by variation of the coupling component used in the diazotization reaction. Table 2 gives a summary of the properties of the major diarylide yellow pigments of commercial significance.

Each of the diarylide yellows offers low-cost, reasonable heat stability, and moderate chemical resistance. The major worldwide market for this class of yellows is the printing ink industry. These yellows are approximately twice as strong as the monoarylide yellows dealt with previously; furthermore, they offer improved bleed resistance and heat fastness. Nevertheless, none of the diarylide yellows have durability properties that would allow for their use in exterior situations and as such should never be considered for an outdoor paint application.

Minor applications in the area of toy enamels and pencil coatings are found for the diarylide yellows, especially if a lead-free formulation is specified.

A range of opacified diarylide yellows is available, having undergone an after treatment that has reduced their surface area and consequently given increased opacity that has resulted in these specific types exhibiting improved fastness properties when compared against their nonopacified counter parts.

Benzimidazolone Yellows

Illustrated in Fig. 21, these yellows take their name from the fact that each features the 5-acetoacetyl-aminobenzimidazolone molecule within its structure. Additionally each is an azo pigment with an acetoacetylarylamide nucleus.

The exceptional fastness to heat, light, and overstriping is attributed directly to the presence of the benzimidazolone group within the pigments structure, first described in 1964 and offered to the marketplace in 1969.

Used initially for the coloring of plastics, these pigments are now finding increased use in the coatings industry where their excellent fastness properties are demanded. Table 3 gives a summary of the properties of this class of pigments.

Heterocyclic Yellows

All these yellow pigments contain a heterocyclic molecule within their structure as shown by the examples presented in Fig. 22. In spite of their apparent complexity, these new high-performance yellows continue to be introduced to satisfy the exacting demands of the coatings industry. Pigments such as Isoindoline Yellow (PY 139) and Quinophthalone Yellow (PY 138) are typical examples of such complex, novel chromophores introduced as recently as 1979 and 1974, respectively.

All of these pigments find application in high-quality coatings where the end use can justify the price of these high-performance products. Table 4 summarizes the properties of

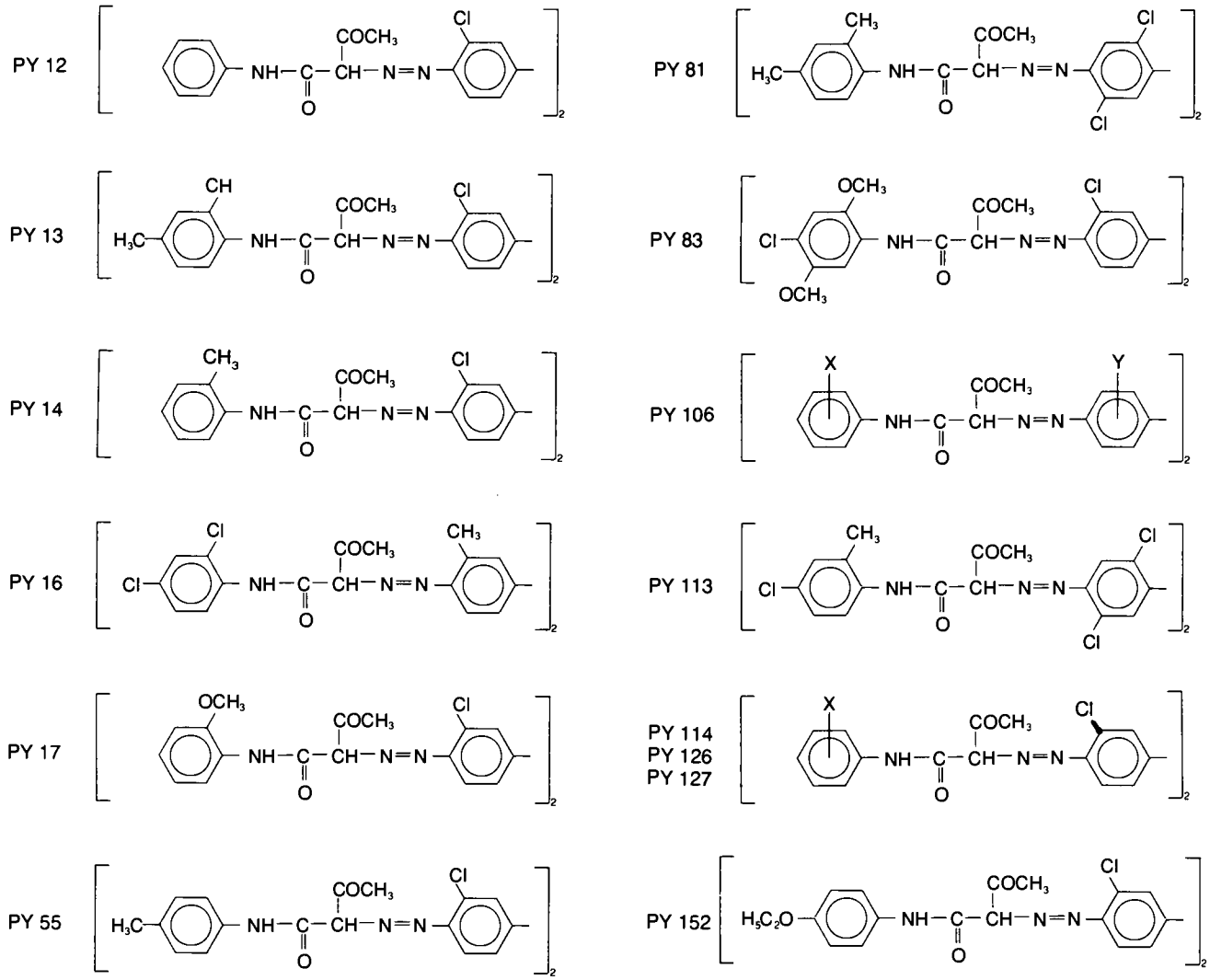


FIG. 20–Structures of the major diarylide yellows.

the heterocyclic yellows currently available that find some use within the coatings industry.

Oranges

Table 5 lists those orange pigments that have significance in todays marketplace.

Azo-Based Oranges

These oranges show considerable variation in structure as can be seen from Fig. 23; all, however, have the azo chromophore (—N=N—) featured within the molecule. The benzimidazolone oranges all feature the azo chromophore in addition to all being produced using 5-acetoacetylaminobenzimidazolone as the coupling agent.

Orthonitroniline Orange—Pigment Orange 2, C.I. Number 12060.

Prepared by the classical diazotization and coupling technique used for all azo pigments, this pigment is the product of coupling diazo orthonitro aniline onto beta naphthol. Its major outlet is in printing inks, and its use is not recommended in coatings due to the pigments poor solvent fastness and lightfastness.

Dinitroaniline Orange—Pigment Orange 5, C.I. Number 12075.

Produced by coupling diazo dinitroaniline onto beta naphthol, this pigment offers good lightfastness in full tone and moderate solvent fastness. As such, Pigment Orange 5 finds outlets in latex paints and air dry architectural and industrial finishes. Its poor baking stability rules out its use in high bake enamels.

Pyrazolone Orange—Pigment Orange 13, C.I. Number 21110.

Synthesized by coupling tetrazotized 3,3′-dichlorobenzidine onto 3-methyl-1-phenyl-pyrazol-5-one, the pigment is a bright, clean yellow shade product that may be used for interior coatings, particularly as a replacement for lead based orange pigments.

Dianisidine Orange—Pigment Orange 16, C.I. Number 21160.

A diarylide orange produced by coupling tetrazotized 3,3′-dimethoxybenzidine onto acetoacetanilide that finds an outlet in baking enamels and interior coatings at full shade.

TABLE 2—Properties of major diarylide yellows.

Colour Index Name	Common Name	Properties
PY 12	AAA Yellow	Poor lightfastness. Poor bleed resistance. Major use in printing inks
PY 13	MX Yellow	Redder shade than PY 12. Improved heat stability and solvent fastness. Major use in printing inks
PY 14	OT Yellow	Green shade. Some use in interior finishes. Poor tint lightfastness
PY 16	Yellow NCG	Bright green shade. Improved heat and solvent fastness. Used in full shade for coatings
PY 17	OA Yellow	Green shade. Some use in interior finishes. Poor lightfastness
PY 55	PT Yellow	Red shade. Some use in interior finishes. Poor lightfastness. Isomer of PY 14
PY 81	Yellow H10G	Bright green shade. Same shade but much stronger than PY 3
PY 83	Yellow HR	Very red shade. Improved transparency, heat stability and lightfastness over PY 12. Some use in interior finishes
PY 106	Yelow GGR	Green shade. Poor tint lightfastness. Major use in packaging inks
PY 113	Yellow H10GL	Very green shade. More transparent than PY 12 and offering better heat and solvent fastness. Some interior finish use
PY 114	Yellow G3R	Red shade. Improved solvent and lightfastness over PY 12. Major use in oil-based inks
PY 126	Yellow DGR	Similar shade to PY 12 but offering improved heat and solvent fastness. Major use in printing inks
PY 127	Yellow GRL	Bright, red shade. Poor lightfastness. Major use in offset inks
PY 152	Yellow YR	Very red, opaque product. Poor lightfastness. Some use in interior finishes as a lead chrome replacement

Tolyl Orange—Pigment Orange 34, C.I. Number 21115.

A diarylide pigment manufactured by coupling tetrazo 3,3′-dichlorobenzidine onto 3-methyl-1-(4′methylphenyl)-pyrazol-5-one. This orange is a bright, reddish shade offering moderate lightfastness and good alkali resistance but poor solvent fastness. As such, the pigment is used in interior coating applications, particularly where a lead-free formulation is specified.

Naphthol Orange—Pigment Orange 38, C.I. Number 12367.

Naphthol Orange is prepared by coupling diazo 3-amino-4-chloro-benzamide onto 4′-acetamido-3-hydroxy-2-naphthanilide to produce a bright red shade orange that exhibits excellent alkali and acid fastness. When used in full shades, this pigment also features acceptable lightfastness. Coatings applications extend to baking enamels, latex, and masonry paints.

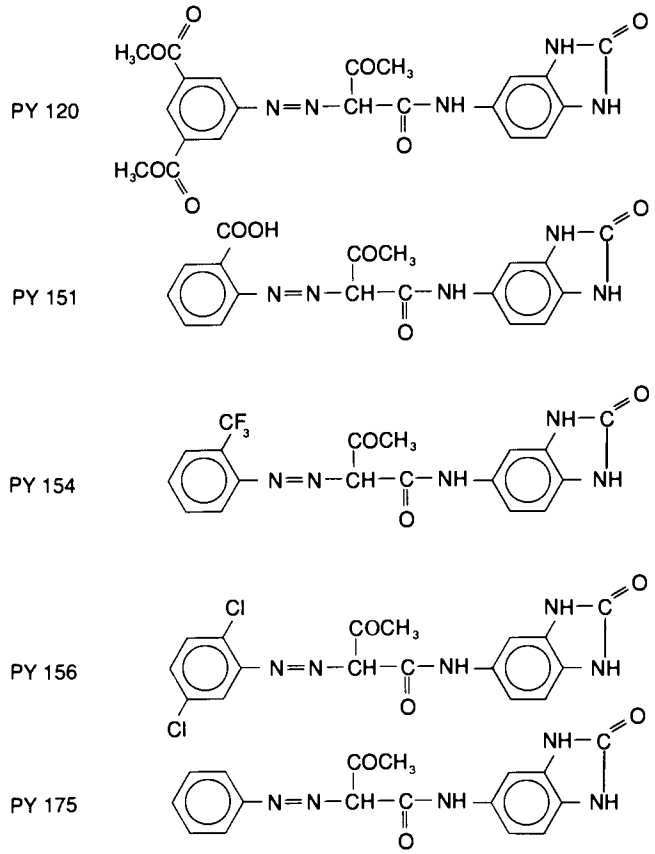


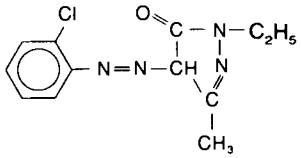
FIG. 21–Structures of the benzimidazolone yellows.

Clarion® Red—Pigment Orange 46, C.I. Number 15602.

TABLE 3—Properties of benzimidazolone yellows.

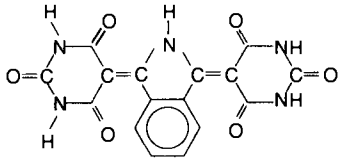
Colour Index Name	Common Name	Properties
PY 120	Yellow H2G	Medium shade. Good solvent fastness. Excellent lightfastness. Used in industrial finishes
PY 151	Yellow H4G	Greener shade. Good solvent fastness. Excellent lightfastness. Industrial and refinish applications
PY 154	Yellow H3G	Green shade but redder than PY 151. Good solvent fastness. Excellent lightfastness. Industrial and automotive refinish applications
PY 156	Yellow HLR	Redder shade. Transparent. Good exterior durability in full shade and tint. All exterior coatings and refinish applications
PY 175	Yellow H6G	Very green shade. Good solvent fastness. Excellent lightfastness. All exterior coatings and refinish applications

PY 60



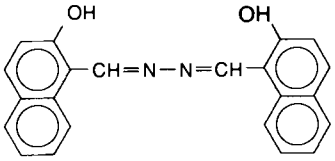
Arylide Yellow

PY 139



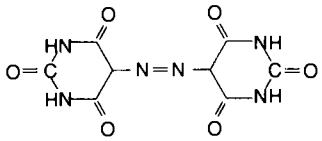
Isoindoline Yellow

PY 101



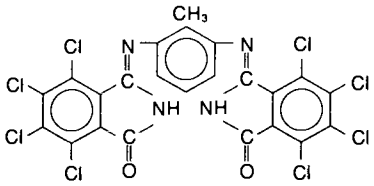
Methine Yellow

PY 150



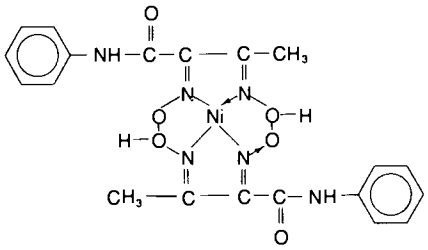
Pyrimidine Yellow

PY 109



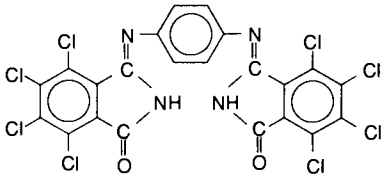
Tetrachloro Isoindolinone Yellow

PY 153



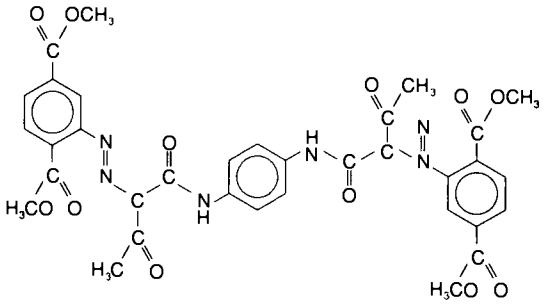
Nickel Dioxine Yellow

PY 110



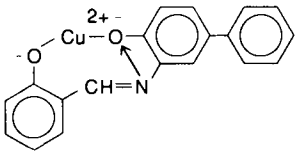
Tetrachloroisoindolinone Yellow

PY 155



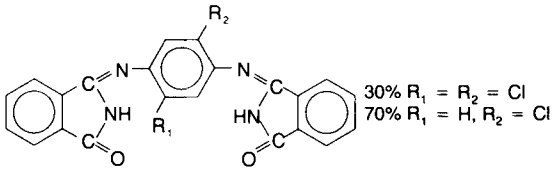
Azo Condensation Yellow

PY 117



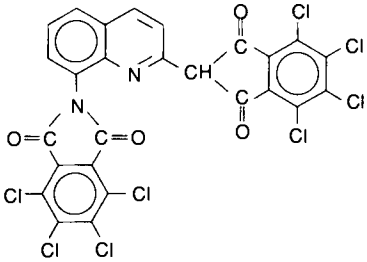
Azomethine Yellow

PY 173



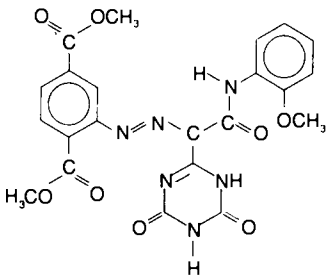
Isoindolone Yellow

PY 138



Quinophthalone Yellow

PY 182



Triazinyl Yellow

FIG. 22–Structures of the heterocyclic and azo condensation yellows.

TABLE 4—Properties of the heterocyclic yellows.

Colour Index Name	Properties
PY 60	Arylide Yellow. Very red shade. Moderate light and solvent fastness. Trade sales, latex, and masonry paints. Good acid and alkali fastness.
PY 101	Methine Yellow, bright yellow. Highly transparent and exceptionally brilliant. Industrial finishes and specialty coatings. Only moderate bleed and alkali fastness.
PY 109	Tetrachloroisoindolinone. Green shade. Excellent brightness strength and durability. Automotive finishes.
PY 117	Greenish yellow copper complex of an azomethine. Excellent chemical, light, and heat fastness. Specialty finishes.
PY 129	Azomethine Yellow, very green shade. Excellent chemical, light, and heat fastness. Industrial and specialty coatings.
PY 138	Green shade Quinophthalone. Clean hue and excellent overall fastness properties. High quality industrial and automotive finishes.
PY 139	Red shade isoindoline. Similar in masstone to medium chrome (PY 34). Excellent light and solvent fastness. Industrial and automotive coatings.
PY 150	Pyrimidine Yellow, very green shade. Good heat and lightfastness. Industrial coatings.
PY 153	Red shade nickel dioxine. Excellent fastness properties. Specialty coatings and baking enamels. Poor acid resistance.
PY 155	Azo Condensation Yellow, green shade. Excellent overall fastness properties in full shade. Industrial and specialty coatings.
PY 173	Isoindolone Yellow, very green shade. Excellent fastness properties. Industrial and specialty finishes.
PY 182	Triazinyl Yellow, medium shade. Excellent fastness properties at masstone levels. Industrial finishes.

A metallized azo pigment manufactured by coupling diazotized 2-amino-5-chloro-4-ethyl benzene sulfonic acid onto beta naphthol followed by reacting this product with barium to yield the barium salt of the pigment. Not recommended for coatings due to its poor lightfastness, inferior alkali resistance, and inadequate solvent fastness, this pigment finds its major outlet in the printing ink marketplace.

Benzimidazolone Orange—Pigment Orange 36, C.I. Number 11780.

The product from the coupling of diazo 4-chloro-2-nitroaniline to 5-acetoacetylamino-benzimidazolone, this is a bright red shade orange of high tint strength. In its opacified form, this pigment offers excellent fastness to both heat and solvents and a hue similar to Molybdate Orange (PR 104). As such, the pigment is used in automotive and high-quality industrial formulations which must be lead free and which were formerly made used the lead-based pigment, Molybdate Orange.

Pigment Orange 60—C.I. Number 11782.

A transparent, yellow shade orange that also exhibits excellent heat and solvent fastness with an exterior durability that allows the pigment to be used in automotive and high performance industrial finishes. Manufactured by coupling benzimidazolone to 4-nitro-aniline.

Pigment Orange 62—The newest of the benzimidazolone oranges, the structure of this pigment has yet to be made public. Again a yellow shade pigment that has shares the lightfastness properties of PO 36 and PO 60 but offers inferior solvent fastness and exhibits slight bleed in alkaline systems. Currently the pigment is being used in oil-based inks and artists colors; its use in the coatings industry has still to be fully explored.

Miscellaneous Oranges

Figure 24 illustrates the structures of those oranges that fall into a "miscellaneous" category as far as such structures have been declared. Table 6 summarizes the properties of this series of pigments, each of which is finding increased use within the coatings industry.

Greens

Copper Phthalocyanine Green

When a self shade green is required, rather than a green produced by mixing blue and yellow, then copper phthalocyanine is the green of choice. This pigment is based upon halogenated copper phthalocyanine using either chlorine or a mixture of chlorine and bromine, the former product being Pigment Green 7 and the later, Pigment Green 36.

Pigment Green 7 is a blue shade green made by introducing 13–15 chlorine atoms into the copper phthalocyanine molecule, whereas Pigment Green 36 is a yellow shade green based upon a structure that involves progressive replacement of chlorine in the phthalocyanine structure with bromine. Fig-

TABLE 5—Orange pigments of significance in the coatings industry.

Colour Index Name	Colour Index Number	Chemical Type
PO 2	12060	Azo
PO 5	12075	Azo
PO 13	21110	Bisazo
PO 16	21160	Bisazo
PO 31	20050	Bisazo condensation
PO 34	21115	Bisazo
PO 36	11780	Benzimidazolone (Azo)
PO 38	12367	Azo
PO 43	71105	Perinone
PO 46	15602	Azo
PO 48	n/a[a]	Quinacridone
PO 49	n/a	Quinacridone
PO 51	n/a	Pyranthrone
PO 52	n/a	Pyranthrone
PO 60	11782	Benzimidazolone (Azo)
PO 61	11265	Tetrachloroisoindolinone
PO 62	11775	Benzimidazolone (Azo)
PO 64	12760	Heterocyclic Hydroxy
PO 67	12915	Pyrazoloquinazolone

[a]n/a = Not assigned.

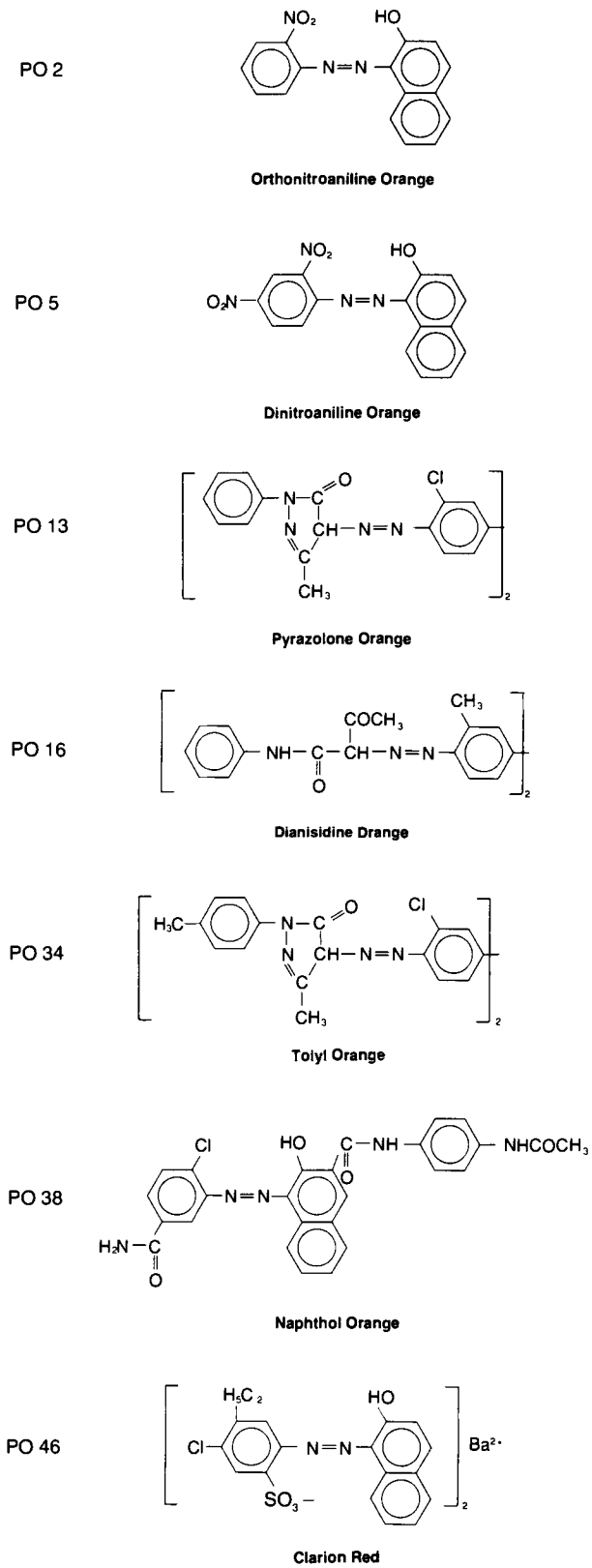


FIG. 23–Structures of the azo-based oranges.

ure 25 illustrates the proposed structures of the phthalocyanine greens. The most highly brominated product, Pigment Green 36, sometimes referred to as "green 6Y" or "green 8G," has an extreme yellow shade and contains 12–13 chlorine atoms.

Both greens exhibit outstanding fastness properties to solvents, heat, light, and outdoor exposure. They can be used equally effectively in both masstone and tints down to the very palest depth of shades. Metallic automotive paints may feature phthalocyanine green at all shade depths. Approximately 50% of the worldwide production of copper phthalocyanine green is consumed by the coatings industry.

Miscellaneous Greens

Table 7 gives a brief summary of the properties of other commercially available organic green pigments that may find some use in the coatings industry. Such inorganic greens as Brunswick Green (PG 15) and Phthalo Chrome Green (PG 13), widely used in industrial coatings, are now being replaced by the more economic organic greens such as phthalocyanine green.

Pigment Greens 1, 2, and 4 are triphenyl-methane-based dyes complexed with phospho tungsto molybdic acid (PTMA) to allow their use as pigments. Their fastness properties are inadequate for most paint applications.

Pigment Green 8, the bisufite complex of 1-nitroso-2-naphthol reacted with ferrous sulfate and then with sodium hydroxide is one of the oldest chelate-based pigments that maintains some minor commercial significance as a colorant for cement. Exhibiting excellent alkali stability this pigment suffers from poor acid fastness.

Pigment Green 10, Nickel Azo Yellow, or Green Gold is the most lightfast azo pigment currently in commercial production, being lightfast at all range of shade from deep tones to pale tints. The pigments does, however, show poor overstripe fastness when used in baking enamels.

Health and Environmental Concerns

The majority of pigments used within the coatings industry are classified as "nuisance dusts" under controlling OSHA standard 29 CFR 1910.1000 with an 8-h time-weighted average exposure tolerance of 15 mg/m^3. Most pigments dealt with in this chapter can be handled in the workplace using normal standard practices of good industrial hygiene as associated with dusty products. However, there are instances which call for specific comment since additional information is available or more specific handling controls are required.

Calcium and Barium Lithol Red, Lithol Rubine, and the BON Reds have each been tested extensively for any toxic properties. The LD_{50} (rat) for each was estimated at greater than 5000 mg/kg. The pigments are classed as nonhazardous as defined by OSHA 29 CFR 1916.25 and not toxic as defined by FHSA 16 CFR 1500.3. BON Maroon has an oral LD_{50} (rat) of 10 g/kg. Additionally, in vitro screening tests for mutagenicity proved negative.

Toxicological results for both Pigment Violet 19 and Pigment Red 122 have been reported. Both pigments exhibited an oral LD_{50} (rat) of 5000 mg/kg or higher. The pigments are thus classified as "non-toxic" under FHSA 16 CFR 1500:3.

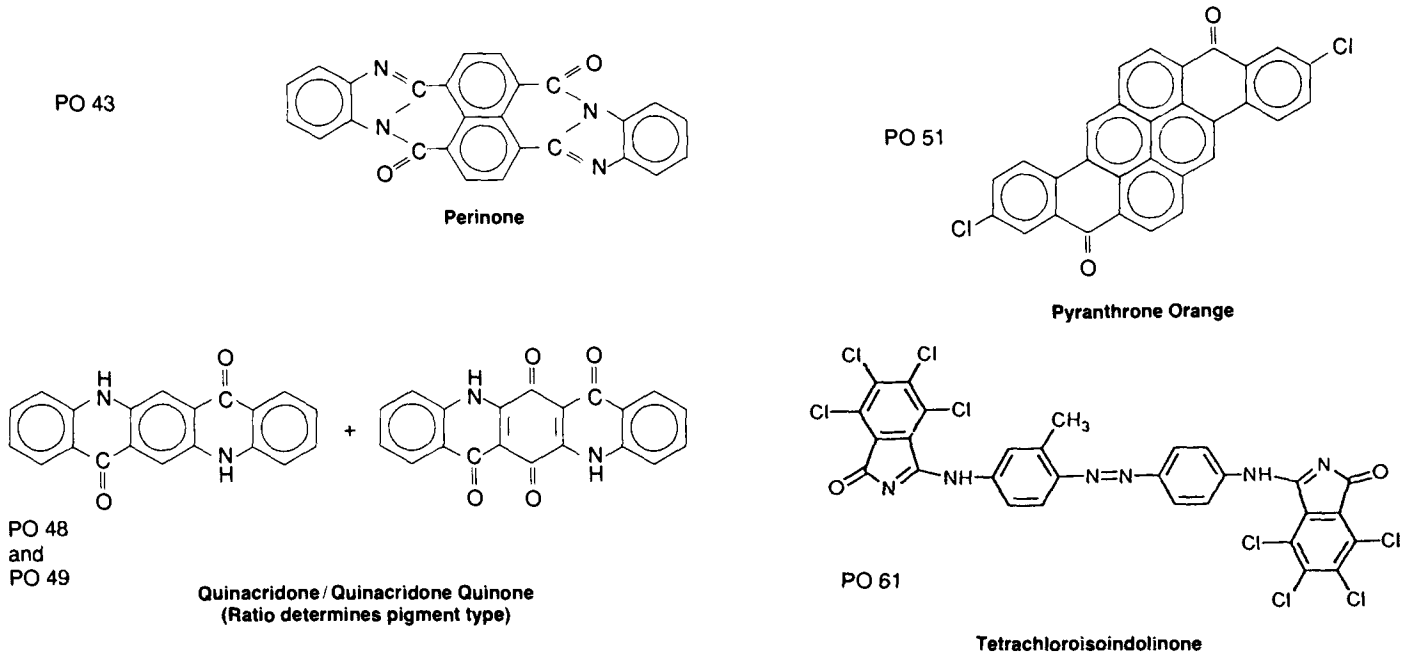


FIG. 24–structures of the miscellaneous oranges.

TABLE 6—Properties of the miscellaneous orange pigments.

Colour Index Name	Properties
PO 43	Perinone. Red shade. Strong clean vat pigment with excellent fastness properties. Used in metallized finishes and high grade paints. Shows slight solvent bleed
PO 48	Quinacridone gold. Yellow shade. Excellent lightfastness. Lacks brightness in masstone. Used in metallic finishes
PO 49	Quinacridone deep gold. Red shade. Dull masstone. Excellent durability. Used in metallics
PO 51	Pyranthrone orange. Medium shade. Excellent solvent, light, and heat fastness. Dull in tint. Exhibits slight solvent bleed. Used in air dry and bake enamels
PO 52	Pyranthrone orange, red shade. Vat pigment with excellent solvent, light, and heat fastness. Dull in tints. Slight solvent bleed. Used in air dry and bake enamels
PO 61	Tetrachloroisoindolinone orange. Medium shade. Exhibits some solvent bleed. Used in metallic automotive finishes
PO 64	Bright red shade. Excellent solvent and lightfastness. Used in industrial coatings
PO 67	Yellow shade. Excellent brilliance in full shade. Good gloss retention. Very good weather and light fastness in full shade. Used in industrial and automotive coatings

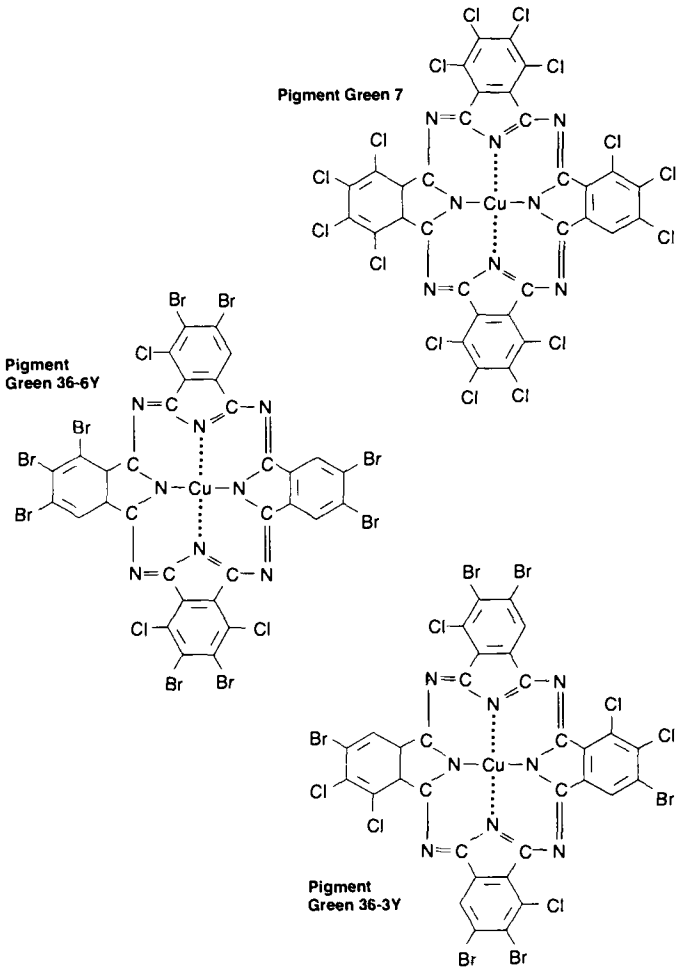


FIG. 25–Proposed structures for phthalocyanine greens (PG 7 and PG 36).

TABLE 7—Properties of the miscellaneous commercial green pigments.

Colour Index Name	Chemical Name	Properties
PG 1	Brilliant Green (Triphenylmethane PTMA)	Brilliant, blue shade. Poor alkali and soap resistance, solvent bleed, and lightfastness. May be used in interior finishes
PG 2	Permanent Green (Triphenylmethane PTMA)	Blend of Pigment Green 1 and Pigment Yellow 18. Bright yellow shade. Poor fastness overall
PG 4	Malachite Green (Triphenylmethane PTMA)	Bright, blue shade. Poor fastness properties overall
PG 8	Pigment Green B (Nitroso)	Yellow shade. Dull hue. Poor fastness properties. May be used in interior emulsions
PG 10	Green Gold (Nickel azo complex)	Yellow shade. Loses metal in strong acid or alkali. Good lightfastness. Moderate solvent fastness. Used in automotive and exterior paints

Additionally, the pigments are classified as being "non-hazardous" as defined by OSHA 29 CFR 1916.25.

Both the disazo condensation pigments and the novel high-performance reds have such low biodegradability that they do not pose any significant risk to either health or to the environment.

In the 1970s it was discovered that the use of trichlorobenzene as a solvent in the manufacture of copper phthalocyanine crude resulted in the formation of poly chlorinated biphenyls (PCBs), principally hexachlorobiphenyl. More modern manufacturing techniques now produce a crude with levels of PCBs significantly below the 25 ppm maximum required by the Environmental Protection Agency (EPA).

The National Toxicological Program examined copper phthalocyanine blue in their long-term bioassay program, and in an almost unprecedented move the pigment was withdrawn from further testing after only 90 days since it failed to exhibit any toxic characteristics during this time period.

Both Pigment Yellow 1 and 74 have been assessed as negative when evaluated in "in vitro" screening tests for mutagenicity.

The industrial handling of diarylide yellows has been the subject of considerable investigation as a result of the relationship of the 3,3′-dichlorobenzidine to the known carcinogen, benzidine. As a result, in the United States, 3,3′-dichlorobenzidine and its salts are classified as an "industrial substance suspected of carcinogenic potential for man" by the ACGIH and as a "cancer suspect agent" by the OSHA (Std. 29 CFR 1910.1007).

In a report of health studies on diarylide yellow pigments, no carcinogenicity was reported from Pigment Yellow 12, 16, or 83 in a two-year feeding study using rats and mice. An oral feeding study using rabbits showed no reduction of the pigments to the parent amine, 3,3′-dichlorobenzidine, during metabolism.

Both Orthonitroaniline Orange and Dinitroaniline Orange are considered to have an oral LD_{50} of greater than 5000 mg/kg (rat) and are therefore classified as "non-toxic" as defined by FHSA 16 CFR 1500.3 and as "not hazardous" under OSHA 29 CFR 1916.3. Both pigments meet the heavy metal content specification under USAST Z66.1-1964 making their use in toy enamels and crayons acceptable.

Pigment Orange 46 contains 15% barium as part of its chemical makeup and as such must be checked for water soluble barium under ANSI Z66.1 prior to it being used in toy enamels and similar coatings.

The LD_{50} for phthalocyanine greens has been shown to be in excess of 2000 mg/kg and the pigments can, therefore, be assumed as not harmful by ingestion. Ninety-day feeding trials with both rats and mice showed no adverse effects nor evidence of adsorption of the pigment. Mutagenicity tests have also proved negative. Concerns about the contamination of phthalocyanine greens with polychlorinated biphenyls (PCBs) have all but disappeared with pigments manufactured within the United States due to today's much improved manufacturing techniques, easily meeting the 25-ppm limit imposed in the United States.

Testing of Pigments for Use in Coatings

Many tests can be applied to a pigment to assess its suitability in a coatings formulation. However, it is of paramount importance that the formulator is satisfied that the tests have a clear relationship to the end use of the coating. It is pointless to evaluate a pigments interior performance only to then use the pigment in an exterior application. For a pigment to be merely the shade and opacity as required by the customer is not an adequate safeguard that the pigment will perform as expected once the product is employed in its intended end use. In today's marketplace, more than any other time in the past, with quality relationships being of such commercial significance, it is vital that the user and supplier have a full understanding of what is expected of any coatings formulation that is in commercial production. The coatings business is under constant change and review and it is in this atmosphere of change that care must be taken to ensure "fitness for use" of any colored organic pigment is fully explored.

Many types of test will be run on a pigment that are not specific to an application but which are a property of the pigment in question and which need to be known in spite of the end use application.

Color and Tint Strength (ASTM D 387-60)

The most obvious property of a pigment is its hue, that is, its color as being distinctly blue, yellow, green, red, etc. and the finer detail that distinguishes a green shade blue from a red shade blue. The other tinctorial properties may be taken as those that are significant when the pigment is used in full tone and those of significance when the pigment is used in reduced shades after diluting the full shade with an opaque white.

Evaluation of any pigment must include a test of full color or masstone that requires inspection of the pigment,

undiluted with white, but fully dispersed in a medium that has relevance to the coatings formulation. Inspection of this full color shows the hue, intensity, transparency, cleanliness, and jetness of the pigment. Comparison of this using side-by-side evaluation with a standard or specification full color will show how close the test pigment comes to the standard. The full color can then be tinted with a white base such as one made from titanium dioxide to enable the pigment's tinting strength to be assessed against a previously approved standard or control. Such a tint is known a bleached, tinted, or reduced drawdown or display.

Oil Absorption (ASTM D 281-31)

A broad definition of oil absorption is the amount of an oil or vehicle which produces a uniform paste when thoroughly incorporated with the test pigment. For standard purposes it is the amount of refined linseed oil, by either weight or volume, necessary to produce a coherent paste from 100 g of dry pigment. Since the transition point of going from a partially wetted powder to an coherent paste is not a clearly defined measure, this test will always be subject to differences between labs and technicians as to when the test's end point is reached. The figure for oil absorption is used by many coatings formulators to give an indication of what effect different pigments will have on the flow properties of the system and to calculate the pigment loading limits. The values are essentially a measure of particle shape, as a pseudospherical particle will have a lower oil absorption than an anisotropic particle.

Bleed Test (ASTM D 279-73)

This test gives an indication of the extent to which the pigment will dissolve, however minutely, in the solvents the pigment is likely to be exposed to during its use. Additionally, an overstripe test can be incorporated where the coating containing the pigment under test is overstriped with a white paint and allowed to dry. The extent of the discoloration of the white is an indication of the pigment's overstripe bleed.

An attempt can be made to quantify this bleed by use of the "Grey Scale for Assessing Change in Color" (B.S. 2662) where the bleed is rated from 5, representing no visible bleed, to 1, representing considerable bleed.

Fastness Tests

The term "fastness" is used in this context to relate to how susceptible or durable a pigment is to the parameter under test. As such, the pigments fastness to light, heat, solvents, etc. can all be measured and quantified using a "Fastness Scale" which rates a pigment from 1 (poor) to 5 (excellent) in all cases except lightfastness which is subdivided into 1 through 8, 1 being total failure to 8 being outstanding.

Among those properties important to the formulator are fastness to solvents, where bleeding is observed by allowing a quantity of the dry pigment to stand for 24 h in contact with a solvent and observing any discoloration of the solvent that occurs, fastness to heat, where the effect of stoving temperatures on the pigment formulated into a finished coating are observed, fastness to acidic or alkaline environments and fastness to light, where several tint levels of a formulation are exposed in such artificial sources as the Xenon or carbon arc fade-ometer (ASTM D 822: Practice for Conducting Tests on Paint and Related Coatings and Materials Using Filtered Open-Flame Carbon-Arc Light and Water Exposure Apparatus) to assess the pigment's behavior in accelerated exposure using the "Blue Wool Scale" to calibrate the measuring equipment (B.S. 1006).

Exposure Testing

It is now generally accepted within the coatings industry on a worldwide basis that the true test of a high-performance pigment is through prolonged outdoor exposure at specifically chosen sites in the state of Florida. To this end, many commercial establishments exist in the state that will provide a controlled service to expose sprayed panels of pigmented coatings angled in a predetermined way towards the sun for periods up to five years with assessments at intervals during this five-year period. Typically many duplicate panels will be exposed per test with a panel being returned to the formulator every six months such that a measure of the system's weatherability as a function of time is maintained on record for each pigment and each system used in outdoor situations.

Specific Gravity (ASTM D 153: Test Methods for Specific Gravity of Pigments)

Defined as the mass of a given volume of a substance as compared to the mass of an equal volume of water at a prespecified temperature, the specific gravity of a pigment is used to arrive at a bulk density or "bulking volume" of the pigment. This is a subjective test that cannot be exactly compared between technicians and between laboratories.

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22

Inorganic Colored Pigments

by Peter A. Lewis[1]

CLASSIFICATION OF INORGANIC PIGMENTS BY CHEMISTRY

BROADLY SPEAKING, the colored inorganic pigments are either lead chromates, metal oxides, sulfides, or sulfoselenides with a few miscellaneous pigments such as cobalt blue, ultramarine blue, iron blue, and bismuth vanadate yellow. This section describes the chemistry, manufacture, and properties of each of these classes of inorganic pigments. Inorganic whites such as zinc oxide, titanium dioxide, lithopone, and zinc sulfide, while pigmentary in nature and most definitely a part of the coatings industry, fall outside of the scope of this chapter.

By chemistry inorganic pigments can be subdivided as shown in Table 1. In addition to the inorganic pigments listed in Table 1, there also exist a series of pigments classed as mixed metal oxides such as, for example, zinc iron chromite brown (PBr 33), cobalt chromite green (PG 26), cobalt titanate green (PG 50), and cobalt aluminate blue (PB 28 and PB 36). These types of inorganic pigments are sometimes also called ceramic colors because of their widespread use in the ceramics industry. Since they are covered in the next chapter of this book, no additional consideration will be given to these colors in this chapter.

CLASSIFICATION OF PIGMENTS BY COLOR

Most likely, when searching for a color to fulfill a particular specification, the coatings formulator is likely to begin the search on the basis of color rather than chemistry. Accordingly, the remainder of this section will concentrate on the classification of inorganic pigments based upon their color rather than their chemistry.

Reds

Iron Oxide Reds

Available as both natural and synthetic products, these pigments also carry such names as haematite, Mars Red, Ferrite Red, Rouge, Turkey Red, and Persian Gulf oxide.

Synthetic iron oxide makes up the largest volume of manufactured iron oxides and is produced by one of four major syntheses:

1. By calcining iron sulfates.

$$12FeSO_4 \cdot H_2O + 3O_2 \longrightarrow 2Fe_2O_3 + Fe(SO_4)_3 + 12H_2O$$

2. From synthetic black oxide by calcining the material in a controlled atmosphere containing oxygen.

$$4FeO \cdot Fe_2O_3 + O_2 \longrightarrow 6Fe_2O_3$$

3. Precipitated red oxide can be prepared in an aqueous medium by growing seed nuclei in the presence of a ferrous salt and scrap steel, the lightness/darkness of the resulting pigment being determined by the crystal size distribution of the precipitate.
4. By calcining synthetic yellow iron oxide to give the dehydrated product, Fe_2O_3.

The wide range of red iron oxide shades available, in addition to their acid and alkali resistance and their economy, accounts for the large volume of these pigments used in today's coatings marketplace.

Molybdate Orange

This pigment is, in fact, Pigment Red 104, a very yellow shade of red that has the common name of molybdate orange, a pigment based upon oxides of lead, chromium, and molybdenum with the empirical formula of $PbCrO_4 \cdot xPbMoO_4 \cdot yPbSO_4$, a solid solution of lead chromate, lead molybdate, and lead sulfate.

Molybdate orange is produced by the addition of a solution of sodium chromate, sodium molybdate, and sodium sulfate under carefully controlled conditions into a solution of lead nitrate at a temperature between zero and 40°C to precipitate the mixed crystal. Control of particle size, particle-size distribution, and crystalline shape combine to determine the actual hue of the pigment, from a red shade of yellow to a red shade of orange with specialty hues such as "chili red."

An opaque pigment with high solvent fastness, moderate heat fastness, and good economy, molybdate orange finds its major outlet in the coatings industry, particularly industrial finishes. On the negative side, the pigment has poor alkali and acid resistance; nontreated grades also tend to darken markedly on prolonged exposure to the environment. Additionally, the pigment is based upon lead, which has been under an "environmental cloud" for some years, a fact which has resulted in molybdate orange being replaced by more expensive, but less toxic, organic reds in decorative paints and almost all original equipment manufacturer (OEM) automotive paints made in the United States.

[1]Coatings Industry Manager, Sun Chemical Corp., Colors Group, Cincinnati, OH 45232.

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TABLE 1—Summary of colored inorganic pigments.

LEAD CHROMATES	
Pigment Yellow 34 $PbCrO_4 \cdot xPbSO_4$	Primrose, medium and dark chrome yellow
Pigment Red 104 $PbCrO_4 \cdot xPbSO_4 \cdot yPbMoO_4$	Molybdate orange
Pigment Orange 21 $PbO \cdot xPbCrO_4$	Light and dark chrome orange
Pigment Green 15 $PbCrO_4 \cdot xPbSO_4 \cdot yFeNH_4Fe(CN)_6$	Chrome green (mixture of lead chrome and iron blue)
METAL OXIDES	
Pigment Yellow 42 Pigment Yellow 43 $Fe_2O_3 \cdot xH_2O$	Yellow iron oxide—synthetic Yellow iron oxide—natural
Pigment Red 101 Pigment Red 102 Fe_2O_3	Red iron oxide—synthetic Red iron oxide—natural
Pigment Brown 6 Pigment Brown 7 Fe_2O_3	Brown iron oxide—synthetic Brown iron oxide—natural
Pigment Green 17 Cr_2O_3	Chromium oxide green
Pigment Green 18 $Cr_2O_3 \cdot 2H_2O$	Chromium oxide green, hydrated
SULFIDES AND SULFOSELENIDES	
Pigment Yellow 35 $CdS \cdot xZnS \cdot yBaSO_4$	Lithopone, cadmium yellow
Pigment Yellow 37 CdS	Cadmium yellow
Pigment Orange 20 $CdS \cdot xCdSe \cdot yBaSO_4$	Cadmium lithopone orange
Pigment Red 108 $CdS \cdot xCdSe$	Cadmium red
MISCELLANEOUS TYPES	
Pigment Blue 27 $Fe(NH)_4Fe(CN)_6 \cdot xH_2O$	Iron or milori blue
Pigment Blue 28 $CoAl_2O_4$	Cobalt blue
Pigment Blue 29 $Na_{6-8}Al_6Si_6O_{24}S_{2-4}$	Ultramarine blue
Pigment Violet 16 $MnNH_4P_2O_7$	Manganese violet
Pigment Yellow 184 $4BiVO_4 \cdot 3Bi_2MoO_6$	Bismuth vanadate/molybdate yellow

Cadmium Red

Cadmium sulfoselenide red, Pigment Red 108, is a solid solution of cadmium sulfide and cadmium sulfoselenide produced by calcining co-precipitated cadmium sulfide and sulfoselenide. the pigment's hue is determined by the amount of cadmium sulfoselenide incorporated into the solid solution and, to a lesser extent, the temperature of processing. Pigment Red 108:1 is a co-precipitate with barium sulfate having the empirical formula

$$CdS \cdot xCdSe \cdot yBaSO_4$$

Cadmium red features excellent stability to heat, alkali, solvents, and light when used at high tint and masstone levels. The pigment offers the formulator a clean bright red with high chroma. Use of the pigment in a reduced form as a light tint is not recommended since the durability will suffer at weak tint levels.

Mercury Cadmium Red

Pigment Red 113 is yet another calcined co-precipitate. It is mercuric sulfide co-precipitated with cadmium sulfide to give a pigment with the empirical formula $CdS \cdot xHgS$, offering good hiding properties and good solvent resistance with excellent brightness, but the pigment's inferior heat and acid resistance when compared to Pigment Red 108 has limited its use in coatings applications.

Violets

Technically blue shade reds, the two most important inorganic violet pigments are Pigment Violet 15, ultramarine violet, prepared by the oxidation of ultramarine blue, Pigment Blue 29, and Pigment Violet 16, manganese violet, prepared when manganese dioxide and diammonium phosphate are slurried at high temperatures in phosphoric acid.

Ultramarine violet has good heat and light fastness and a brilliant red shade. The pigment will react with metals to form sulfides and finds use in cosmetic applications and specialty acrylic poster paint and artists colors.

Manganese violet does not possess the same brightness of hue as Pigment Violet 15 and has only moderate opacity and poor alkali resistance. On the plus side, the pigment has high lightfastness and superior fastness to solvents and overstripe bleed. Major uses are in the plastics and cosmetics industry.

Blues

Iron Blue

Also known as Prussian Blue and Milori Blue, this pigment is manufactured by reacting ferrous sulfate and sodium ferrocyanide in the presence of ammonium sulfite to yield a leucoferricyanide called Berlin White, which is then isolated and dissolved in sulfuric acid and oxidized with sodium chlorate to yield iron blue.

$$Na_4Fe(CN)_6 + FeSO_4 + (NH_4)_2SO_4 \longrightarrow Fe(NH_4)_2Fe(CN)_6 + 2Na_2SO_4$$

(Berlin white)

$$6Fe(NH_4)_2Fe(CN)_6 + 3H_2SO_4 + NaClO_3 \longrightarrow 6FeNH_4Fe(CN)_6 + NaCl + 3(NH_4)_2SO_4 + 3H_2O$$

Differing grades of iron blue exist that offer varying masstone, strength, oil absorption, and dispersion characteristics. Chinese Blue, for example, offers a greener undertone, whereas Bronze Blue features a surface bronziness effect that varies dependent upon the viewing angle.

Iron blue offers good resistance to weak acids but markedly poor resistance to even mild alkali; furthermore, the pigment has a tendency to "bleach out" on storage, losing almost all its color when incorporated into a paint formulation that contains oxidizable vehicles such as linseed oil. The pigment has only acceptable lightfastness properties when used at

masstone levels; extension of the paint with a white such as titanium dioxide gives a weak blue tint that will rapidly fade on exposure.

Ultramarine Blue

Going by such varied common names as Laundry Blue, Dolly Blue, and lapis lazuli, this pigment, made by the controlled grinding of a mixture of calcined kaolin, soda ash, sulfur, coal, and sodium sulfate, is Pigment Blue 29. Empirically the product is $Na_6Al_6Si_6O_{24}S_4$, and its major use is as a component of laundry powders and detergent soaps. Less than 5% of the production is used in the coatings industry for interior emulsion paints that require high alkali resistance and lightfastness.

Yellows

Strontium Yellow

Strontium chromate, $SrCrO_4$, prepared by precipitating a suitably soluble chromate with an appropriate strontium salt, is Pigment Yellow 32. Finding a primary use in corrosion-inhibiting coatings, this pigment has poor tint strength, low opacity, and unsatisfactory alkali and acid resistance, which limits its more widespread use in the coatings industry.

Chrome Yellow

A co-precipitate of lead sulfate and lead chromate, Pigment Yellow 34 has the empirical formula $PbCrO_4 \cdot xPbSO_4$. Various types exist that differ in the ratio of the lead sulfate to the lead chromate and as such are described as medium chrome, primrose, and lemon chrome yellows. A typical primrose chrome will contain 23 to 30% lead sulfate in the solid solution of the co-precipitate, whereas a medium chrome will contain 0 to 6% lead sulfate. During manufacture, proprietary techniques are employed such that the orthorhombic crystal form is produced almost exclusively in preference to the unstable monoclinic form.

Many different grades of this type of pigment are available to offer such improvements in properties as better chemical resistance, decreased tendency to darken on exposure, improved weathering, and as a silica-encapsulated product to minimize solubility of the lead contained within the pigment.

Primrose chrome exhibits a very green shade and offers good lightfastness, high opacity, and low rheology coupled with economy of use. The coatings industry, closely followed by the ink and plastics industry, is the largest consumer of primrose chrome. Medium chrome is used widely in road-marking paints in the United States where the law requires a yellow marking line as opposed to white. Grades that have been pre-darkened by the use of antimony during the precipitation stage offer much increased stability to weathering since these grades will not darken further on exposure to sulfur in the atmosphere.

Zinc Chromate

Also called zinc yellow, this pigment is identified as Pigment Yellow 36, as opposed to the lithopone version incorporating barium sulfate which is Pigment Yellow 36:1. It is a bright, green shade of yellow made by the precipitation of hydrated zinc potassium chromate from the reaction of sodium bichromate with zinc oxide and potassium chloride. The lithopone version is merely a co-precipitate of zinc chromate onto barium sulfate to give an extended pigment that carries the Colour Index name of Pigment Yellow 36:1.

Used primarily in corrosion-inhibiting coatings, its poor tinctorial strength and poor resistance to acid and alkali severely limits this pigment's use elsewhere.

Cadmium Zinc Yellow

Yet another solid solution, Pigment Yellow 35 is a cadmium solution co-precipitated with zinc sulfide. Calcination of this product gives pure cadmium zinc sulfide, $CdS \cdot xZnS$. The hue is readily altered by varying the ratio of the two components of this solid solution. Levels of zinc sulfide of 14 to 21% give a green or primrose shade, while 1 to 7% gives a redder shade achieving a golden hue. Incorporation of barium sulfate during manufacture produces a lithopone version, Pigment Yellow 35:1.

Cadmium zinc yellows offer bright, clean, opaque pigments with excellent resistance to heat, light, and strong solvents. Their poor fastness to mineral acids and marked tendency to fade when used at low tint levels limits their use within the coatings industry.

Cadmium Sulfide Yellow

Calcined calcium sulfide, CdS, is identified in the Colour Index as Pigment Yellow 37. This pigment can be produced with hues ranging from a green shade to a very red shade by simply varying the calcination conditions. Offering excellent stability to heat, light, acids, and alkali, this pigment's only major drawback is its tendency to fade in the presence of moisture.

Iron Oxide Yellows

As with most of the commercially available iron oxides, this pigment can be obtained as the natural grade, Pigment Yellow 43, or the synthetic variant, Pigment Yellow 42.

The natural yellow oxides, $FeO \cdot xH_2O$, will also contain clay and various other minor minerals. Available under several names, often related to the country of origin or the pigment's history, the natural yellow oxide is also called Indian Ochre, Ocher, Sienna, and limonite.

The synthetic oxide is produced by direct precipitation using ammonium hydroxide and ferrous sulfate, via the Penniman-Zoph process using scrap steel and a ferrous salt to grow seed particles or by the aniline process where nitrobenzene is reacted with metallic iron to produce iron oxide and aniline. The synthetic product has the empirical formula $Fe_2O_3 \cdot xH_2O$, irrespective of the manufacturing process.

Iron oxide yellows are economical pigments with excellent lightfastness, weatherability, opacity, and flow properties. On the downside, they are dull in masstone and exhibit only fair tinctorial strength and moderate baking stability at best. It is their value in use that has resulted in their widespread acceptance throughout the coatings industry.

Bismuth Vanadate/Molybdate Yellow

The most modern of the inorganic pigments discussed in this section, Pigment Yellow 184, was introduced into the marketplace in 1985. Manufactured by dissolving bismuth nitrate, sodium vanadate, and sodium molybdate in nitric acid followed by the precipitation of a complex mixture of the metals, the precipitate is calcined to give a polycrystalline product, $4BiVO_4 \cdot 3Bi_2MoO_6$. It is a green shade of yellow used

principally for a brilliant solid shade in both automotive and industrial coatings. The pigment has excellent weatherfastness coupled with good hiding power and gloss retention. Earlier grades suffered from the unusual phenomenon where the color under shadows would darken only to lighten again once the shadow was removed. More stable grades introduced recently do not suffer this drawback.

Oranges

Chrome Orange

A basic lead chromate, Pigment Orange 21, is formed under alkaline conditions to give a product of empirical formula $PbCrO_4 \cdot xPbO$, shades varying from a yellow shade to red shade dependant upon the alkalinity maintained during the reaction sequence.

As with all lead-containing pigments, the product will darken on exposure to the atmosphere, the rate dependant upon the sulfur content. The pigment offers low cost and moderate lightfastness and finds use in the protective coatings marketplace with some use as a shading pigment for road traffic paints.

Cadmium Orange

Pigment Orange 20, cadmium sulfoselenide orange, is a solid solution produced by calcining cadmium selenide with cadmium sulfide at approximately 1000°C (1800°F). A change in the ratio of the solid solution components gives pigments that are bright yellow (PY 35) to bright red (PR 108). Barium sulfate added or produced during the processing will form the lithopone grade, Pigment Orange 20:1.

This pigment is used in industrial coatings, for color coding applications, where chemical and heat resistance are principal requirements.

Cadmium Mercury Orange

This pigment is a solid solution of mercury sulfide in cadmium sulfide and is identified as Pigment Orange 23. Again, various hues can be obtained by controlling the formation of the mixed crystal manufactured by precipitating the sulfides of cadmium and mercury from a solution of their soluble salts. Again, the final stage is calcination in an inert atmosphere to give an extremely heat stable pigment with excellent chemical resistance, weatherability, and solvent fastness.

Greens

Chrome Green

These pigments are merely mixtures of a green shade chrome yellow (PY 34) and iron blue (PB 27). As such, Pigment Green 15 offers a range of hues with a light yellow shade to a deep dark shade, providing good hiding, high tint strength, and a moderate chemical resistance at an economical price. It can be used for bake enamels where the bake temperature does not exceed 148°C (300°F), but is restricted to exterior and industrial coatings applications as opposed to decorative finishes because of its lead content.

Chromium Oxide Green

Pigment Green 17 is a pure, calcined chromium oxide, Cr_2O_3, manufactured by reduction of sodium bichromate with carbon or sulfur:

$$Na_2Cr_2O_7 + 2C \longrightarrow CO + Na_2CO_3 + Cr_2O_3$$

This pigment has a unique use in camouflage paints because of its ability to reflect infrared light. Otherwise, the product finds a use where its price can be justified by the resultant excellent light and chemical resistance properties the pigment features.

Hydrated Chromium Oxide Green

Also known as Viridian Green or Guignets green, Pigment Green 18 is a hydrated chromic oxide of formula $Cr_2O_3 \cdot 2H_2O$ from the hydrolysis of the product produced by calcining sodium bichromate with boric acid. The pigment is a bright, blue shade green with high chroma and outstanding fastness properties in both masstone and deep tints.

Browns

Natural Iron Oxides

This is mined from either iron oxide mines operating principally to supply ore as feedstock for blast furnaces with a small offtake directed to the pigment industry or pigment mines which operate solely to supply pigmentary grade ore.

Typically the mined ore is slurried in an aqueous suspension and washed through a series of stages to remove sand and clay after which the slurry passes into a separator tank, then through a Dorr bowl rake where the iron oxide ore is separated and dried as a thin layer on a rotary drum drier. The dried natural ore is then pulverized and classified to produce pigmentary iron oxide. Pigment Brown 7 is an iron oxide brown that is available in shades ranging from light red to deep purple brown. Empirically the product is Fe_2O_3. Metallic brown is produced from calcined hematite (PR 102) and burnt sienna from calcined limonite (PY 43).

Pigment Brown 7:x is a ferrosoferric oxide derived from ores containing 25% manganese dioxide with a distinct composition as $Fe_2O_3 \cdot xMnO$ with varying proportions of clay. Classical names include such as raw umber, burnt umber, and Turkish umber.

Synthetic Brown Oxide

Also known as brown magnetite iron oxide, Pigment Brown 6 is produced by controlled oxidation of Pigment Black 11. Chemically the product may be represented as $Fe_2O_3 \cdot xFeO \cdot yH_2O$.

Pigment Brown 11 is magnesium ferrite from the calcination of a blend of ferric and magnesium oxides, $MgO \cdot Fe_2O_3$.

The volume of all types of brown oxides used in coatings is generally low since most browns are achieved by mixing yellow, red, and black pigments. As a class, these pigments have good chemical resistance and high tint strength and as such find some use in wood stains and furniture finishes.

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23

Ceramic Pigments

by Richard A. Eppler[1]

CERAMIC PIGMENTS ARE COMPLEX MIXTURES of oxygen-containing materials that have been calcined at high temperatures to form specific crystalline phases [*1*]. In most cases, oxide raw materials are carefully mixed and then calcined in either batch kilns or continuous calciners [*2*]. After calcination, they are ground to the necessary fineness in mills. Micronizers and/or jet mills are used to break agglomerates. The final production step involves careful control of the color tone by adjustment with toners.

Because these pigments are formed at high temperatures, they generally offer superb thermal stability and are relatively inert. This results in excellent weathering and light fastness properties. Most of these pigments have superior acid and alkali resistance. They are nonmigrating and nonbleeding in nature and do not interact with polymer systems [*3*].

The principal disadvantage of ceramic pigments is their low tinting strength. In addition, some are relatively high in cost. This is particularly true of cobalt-containing pigments. Some of these pigments are difficult to disperse. However, the recent development of easily dispersed ceramic pigments should eliminate this problem, at least for water-based systems. A final concern is the inherent hardness of these pigments. Their hardness can lead to processing system damage through abrasion. When using ceramic pigments, processing system components designed for use with abrasive materials should be considered.

The major use of ceramic pigments is for applications such as vinyl siding and automotive paints where the product is thermally cured and then placed in an outdoor setting.

CERAMIC PIGMENTS USED IN ORGANIC PAINTS

The major criterion used in selecting ceramic pigments for organic paints is hardness. The pigments listed in Table 1 and discussed below are those that can be used in paint processing equipment without causing excessive wear. Property attributes of the pigments are given in Table 2. All are compatible with most polymer systems, with manganese-doped rutile especially useful when it is necessary to avoid iron.

Nickel-doped rutile, which is often called Sun Yellow, is produced from a mixture of various amounts of titanium (IV) oxide, nickel (II) oxide, and antimony (V) oxide by high-temperature calcination [*1*]. The result is formation of a crystalline matrix of rutile that has the basic chemical formula $(Ti,Ni,Sb)O_2$. The pigment is used for coloring high-performance industrial coatings, wire coatings, vinyl sidings, automotive and other exterior paints, as well as for roofing, granules, porcelain enamels, and ceramic bodies.

Chrome-doped rutile is prepared from a mixture of varying amounts of titanium (IV) oxide, chrome (III) oxide, and antimony (V) oxide by high-temperature calcination [*1*]. The resultant crystalline rutile matrix has the basic chemical formula $(Ti,Cr,Sb)O_2$. The orange-yellow pigment is used for coloring the same systems as nickel-doped rutile.

Manganese-doped rutile is prepared from a mixture of various amounts of titanium (IV) oxide, manganese (II) oxide, and antimony (V) oxide by high-temperature calcination [*1*]. The resulting crystalline rutile matrix has the basic chemical formula $(Ti,Mn,Sb)O_2$. The brown pigment is used for coloring the same systems as nickel-doped rutile.

Spinel brown pigments are an example of the 2-4 inverse spinels [*4*]. The basic pigment is prepared by a high-temperature calcination of titanium (IV) oxide and iron (II) oxide [*1*]. The resulting crystalline matrix of spinel is brown in color and has the basic chemical formula Fe_2TiO_4. The spinel phase permits extensive substitution, within defined limits, with other compounds to provide a variety of shades of brown. Modifiers used for substitution include Al_2O_3, CoO, Cr_2O_3, Fe_2O_3, MnO, and ZnO. The pigments are used for coloring high-performance industrial coatings, wire coatings, vinyl sidings, and automotive and other high-quality exterior paints.

Titanate green and blue-green pigments are also produced by high-temperature calcination of mixtures of titanium (IV) oxide, cobalt (II) oxide, nickel (II) oxide, and zinc (II) oxide to form a crystalline matrix of inverse spinel [*1*]. The pigments have the basic chemical formula $(Co,Ni,Zn)_2TiO_4$. The pigments are used for coloring the same systems as the spinel brown pigments.

Cobalt blue pigments are crystalline spinels formed by high-temperature calcination of cobalt (II) oxide and aluminum (III) oxide in varying amounts [*1*]. The basic cobalt blue pigment (CAS 68186-86-7) has the chemical structure $CoAl_2O_4$. The lighter-colored cobalt blue is prepared by addition of zinc (II) oxide to the ingredients used for the basic pigment. The chemical structure of the resultant material (CAS 68186-87-8) is $(Co,Zn)Al_2O_4$. Blue-green shades are produced by introduction of chromium (III) oxide, partially replacing aluminum (III) oxide in the basic cobalt blue system. It has the chemical formula $Co(Al,Cr)_2O_4$. In addition to being

[1]Eppler Associates, 400 Cedar Lane, Cheshire, CT 06410.

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TABLE 1—Recommended ceramic pigments for use in organic paints.

Ceramic Pigment	Pigment Powder Color	Color Index/Name	CAS Number
Nickel-doped rutile	Yellow	77788/Pigment Yellow 53	71077-18-4
Chrome-doped rutile	Orange-yellow or maple	77310/Pigment Brown 24	68186-90-3
Manganese-doped rutile	Brown	77899/Pigment Yellow 164	68412-38-4
Spinel brown	Brown	77543/Pigment Black 12	68187-02-0
Titanate greens and bluegreens	Green	77377/Pigment Green 50	68186-85-6
Cobalt blue	Blue (basic)	77346/Pigment Blue 28	68186-86-7
Cobalt-zinc blue	Blue (lighter than basic)	77347/Pigment Blue 72	68186-87-8
Cobalt chromite blue	Blue-green	77343/Pigment Blue 36	68187-11-1
Cobalt phosphate violet	Purple	77360/Pigment Violet 14	13455-36-2
Manganophosphate violet	Purple	...	10101-66-3
Ceramic black	Jet black	77428/Pigment Black 28	68186-91-4
Ceramic black	Jet black	66502/Pigment Black 27	68186-97-0

TABLE 2—Properties of recommended ceramic pigments (see Table 1 for color and pigment reference numbers).

Ceramic Pigment	Heat Stability	Weathering Properties	Light Fastness	Acid/ Alkali Resistance	Hydrolytically Stable	Nonmigrating/ Bleed
Nickel-doped rutile	High	Excellent	Excellent	Excellent	Yes	Yes
Chrome-doped rutile	High	Excellent	Excellent	Excellent	Yes	Yes
Manganese-doped rutile	High	Excellent	Excellent	Excellent	Yes	Yes
Spinel brown	High	Excellent	Excellent	Good	Yes	Yes
Titanate greens and bluegreens	High	Excellent	Excellent	Excellent	Yes	Yes
Cobalt blue—basic	High	Excellent	Excellent	Excellent	Yes	Yes
Cobalt zinc blue	High	Excellent	Excellent	Excellent	Yes	Yes
Cobalt chromite blue	High	Excellent	Excellent	Excellent	Yes	Yes
Cobalt phosphate violet	High	Excellent	Excellent	Excellent	No	Yes
Manganophosphate violet	High	Excellent	Excellent	...[a]	No	Yes
Ceramic Jet black	High	Excellent	Excellent	Excellent	Yes	Yes
Ceramic Jet black—stronger	High	Excellent	Excellent	Excellent	Yes	Yes

[a]Manganophosphate violet has good acid resistance, but poor alkali resistance.

used to color the same systems as the rutiles, the cobalt blues are used in ceramic glazes.

Cobalt phosphate violet is prepared by high-temperature calcination of cobalt (II) oxide and phosphorus (V) oxide to form a crystalline phosphate [*1*]. It has the formula $Co_3(PO_4)_2$. It is used for coloring the same systems as the spinels and in printing inks. Manganophosphate violet is produced by a precipitation process from ammonium salts of manganese (III) and phosphorus (V) [*3*]. This pigment has the chemical formula $NH_4MnP_2O_7$. It is used for inks and other applications where heat stability is of less importance.

One ceramic black is a jet black powder produced by calcination of mixtures of copper (II) oxide and chromium (III) oxide to form a crystalline spinel [*1*]. The basic jet black has the formula $CuCr_2O_4$. A marginally stronger black is produced by a high-temperature calcination of cobalt (II) oxide, iron (III) oxide, and chromium (III) oxide in varying amounts, also to form a spinel. The product has the chemical formula $(Co,Fe)(Fe,Cr)_2O_4$. The ceramic blacks are used in the same systems as the above-described rutiles.

Like most pigments, ceramic pigments are manufactured to have a suitable particle size for incorporation into the coating, but when a paint manufacturer receives them in bags of dry material, the particles generally have absorbed moisture [*5*]. They are stuck together in groups by this layer of water or absorbed air. Hence, in the dispersing process, these layers must be destroyed and the primary particles dispersed in the paint.

There are a number of wetting and dispersing agents which can be added to a paint [*5*]. Discussion of this topic will be found elsewhere in this manual. However, one important additional factor should be noted. Most ceramic pigment manufacturers today offer a line of easily dispersed pigments. These products are formulated with a proprietary dispersant. Adding the dispersant to the pigment itself promotes optimum contact between the dispersant and the pigment. These dispersants are primarily designed for water-based systems.

TESTING OF CERAMIC PIGMENTS

Ceramic pigments are usually tested for two important properties—particle size and tinting strength. Hardness is essentially a property of the pigment crystal produced and is insensitive to production details. Hence, handbook values for the crystal are usually adequate for most purposes.

There are three aspects of particle size to be considered: (1) the particle-size distribution; (2) the concentration of coarse particles; and (3) the particle shape as it affects the formulation of the paint. The measurement and reporting of particle-size distribution of pigments in paints is contained in ASTM Practice for Reporting Particle Size Characteristics of Pigments (D 1366) [*6*]. The practice covers measurements by microscopic techniques, sedimentation methods, turbidimetric methods, absorption, and permeability methods. The recent laser dispersion and electric sensing zone techniques are not yet dealt with in this standard. The procedures described in ASTM Test Method for Particle Size Distribution of Alumina or Quartz by Electric Sensing Zone Techniques (C 690) and ASTM Test Method for Determining Particle Size Distribution of Alumina or Quartz by Laser Light Scattering (C 1070) should be applicable to ceramic pigments [*7*].

Determination of the concentration of coarse particles that may cause defects in a coating is covered by ASTM Test Methods for Coarse Particles in Pigments, Pastes, and Paints (D 185) [*6*].

The amount of pigment which may be added to a paint formulation is a strong function of the shape of the pigment particles. Higher loadings are possible for pseudo-spherical particles than is possible with plate-like particles. This property of a pigment is measured by determining the oil absorption characteristics of the pigment as described in ASTM Test Method for Oil Absorption of Pigments by Spatula Rub-out (D 281) [*6*].

Tinting strength is the other important characteristic that needs to be evaluated. The determination of the color of a pigment requires that it be dispersed into a medium similar to that in which it is to be used. It is never acceptable to imply application color from the color of a dry pigment. The techniques for dispersing a pigment in a suitable vehicle and then measuring the color in both masstone and letdown are detailed in ASTM Test Method for Color and Strength of Color Pigments with a Mechanical Muller (D 387) [*6*].

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Extender Pigments

by Henry P. Ralston[1]

COATING FORMULATORS FREQUENTLY USE extender pigments to reduce the raw material cost of a coating formulation and, in some cases, improve coating performance. Extender pigments are relatively inexpensive compared to titanium dioxide or color pigments and are easily incorporated into a coating. Most are white or near-white inorganic minerals, beneficiated to varying degrees, with a coarser particle size and lower oil absorption (binder demand) than primary pigments.

Extender pigments include inexpensive fillers, such as coarse calcium carbonate, which are used to reduce cost by filling coating volume with minimal impact on performance. Other extender pigments such as hydrous and calcined kaolin can actually enhance coating performance plus provide very favorable economics by improving the efficiency of a more expensive pigment such as titanium dioxide.

Some extenders have specific features that improve coating performance, such as better durability, derived from the unique platy particle shape of talc or mica. Pyrogenic, fumed, and diatomaceuos silica are frequently used as functional additives to control rheology and film gloss. While extender pigments can vary in form and use, the added value delivered to the coatings formulator remains [*1–4*].

CALCIUM CARBONATE

Description

Calcium carbonate, also known as calcite, whiting, or limestone, has the chemical formula $CaCO_3$. It is produced by dry or wet grinding of limestone or by precipitation via carbonization of slaked lime. Product from ground limestone is dependent upon both the initial crude mineral and the subsequent degree of processing or beneficiation. Limestone ore is crushed and milled; the dry ground product is air classified to different particle-size fractions. Wet ground product is milled as a slurry, undergoes flotation to remove impurities, and is then filtered and dried. The coarser dry-ground grades of calcium carbonate are used as inexpensive fillers.

Precipitated calcium carbonate is produced by heating natural limestone to form calcium oxide, which is then slaked in water and reacted with carbon dioxide to form a low-solids slurry. The precipitate is vacuum filtered, dried, and ground. Both particle shape and size of precipitated grades can be carefully controlled by altering reaction conditions to yield effective extender pigments. Fine-particle-size precipitated grades and fine-ground limestones are utilized as extender pigments.

Physical Properties

Calcium carbonate products are differentiated further by physical properties such as particle size, brightness, residue, and, for precipitated grades, oil absorption. Fine-particle-size products have an average particle size of from less than 1 to about 4 μm with coarse-particle-size grades ranging up to about 15 μm. Most are high in brightness, ranging from 90 to 98, with a pH of 9 to 10. Ground carbonates have low oil absorption which correlates with low resin demand in coatings.

Coatings Performance

Calcium carbonate is widely used in water-based trade sales architectural coatings since it is less expensive than titanium dioxide, a primary pigment in paints and coatings, and significantly lowers raw material cost. Fine-particle-size calcium carbonate functions as an extender by spacing titanium dioxide and maintaining or improving optical properties of the dry coating film at lower titanium dioxide levels. Higher-oil-absorption (binder demand) precipitated grades may contribute to opacity. Finer-particle-size grades tend to develop high gloss; high brightness can have a positive effect on the color of the coating.

Coarser grades of calcium carbonate are primarily used as fillers to reduce cost but also contribute to flatting and enhance low sheen control. Some grades may cause frosting and chalking in exterior applications.

KAOLIN

Description

Kaolin, also known as china clay, is an aluminum silicate with the chemical formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, which is commercially available in both hydrous and calcined (anhydrous) forms. Domestic deposits occur primarily in South Carolina and Georgia. It has a platy particle shape with finer particles present as individual platelets and coarse particles present as stacks of platelets or booklets.

[1]Technical Service Engineer, Engelhard Corporation, 101 Wood Avenue South, Iselin, NJ 08830.

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The hydrous form is produced by air flotation or water washing. Air-floated grades are crushed and ground to a specific particle size and air classified. This process is very dependent on the initial ore deposit.

Water washing involves processing the mineral in an aqueous slurry and separating particles of different size, which can then be recombined to yield products with controlled particle-size distribution. These products can also be further beneficiated by bleaching, ozonation, high-intensity magnetic separation (HIMS), or chemical flotation to remove impurities and improve color. Some grades are subjected to a delaminating process that physically separates coarse platelets from one another.

Water washing offers a more carefully controlled product available in either slurry or dried form. Predispersed spray-dried beads offer ease of handling and are suitable for water-based coating systems. Pulverized, acid grades are recommended for solvent-based coatings.

Calcined (anhydrous) forms are produced by subjecting hydrous kaolin to thermal dehydroxylation, which removes the water of crystallization and alters the crystal shape.

Physical Properties

Kaolins are also differentiated by properties such as particle size, brightness, residue, and oil absorption. Hydrous kaolins have an average particle size ranging from an extremely fine 0.2 up to 5 μm depending on the product. Dry brightness ranges from 85 to 90%, and most water-washed grades are very low in residue. Acid grades have a pH of 4 to 5, while predispersed grades are 6 to 7. Kaolins are chemically inert. Water-washed grades are lower in impurities such as soluble salts than are air-float grades.

Calcined grades range from below 1 to 2.5 μm in average particle size and are usually higher in brightness than all except premium hydrous grades. These grades have a more irregular particle shape and higher oil absorption than the hydrous grades.

Coatings Performance

Fine particle-size hydrous kaolins are commonly used in latex and alkyd trade sales paint. Finer particle size improves opacity and allows for cost reduction by extending/reducing the amount of titanium dioxide. Finer particle-size products also develop higher gloss and are particularly useful in enamels and semigloss formulations. Chemically modified hydrous kaolins are effective in high-solids and water-reducible industrial coatings.

Delaminated grades also develop good opacity, and the platy particle shape improves barrier resistance and film integrity. Delaminated grades or coarser hydrous grades are more suitable for exterior trade sales formulations and exhibit more controlled chalking and better overall durability. Air-floated grades are not used significantly in coatings because the higher water-soluble salt content can cause viscosity instability.

Calcined kaolins are widely used in interior latex and alkyd trade sales flats to develop dry hiding and reduce cost at lower titanium dioxide levels. Dry hiding is due to the higher oil absorption (binder demand) of the calcined grades, resulting in more air/pigment and air/binder interfaces in the dry paint film. These grades develop good flatting, and the harder calcined particles also improve scrub resistance in interior latex coatings [*5,6*].

TALC

Description

Talc is a hydrated magnesium aluminum silicate with the chemical formula $3MgO{\cdot}4SiO_2{\cdot}H_2O$. Deposits are found domestically in New York, Vermont, Montana, Texas, and California. Talc varies widely in purity depending on its source and may also contain dolomite, limestone, and silica, among others. Western talcs are highly platy, while eastern talcs have an acicular particle shape. Both dry and wet grinding techniques are used in its beneficiation. Ore flotation processes are used to produce high-quality products. Dry processing includes use of jaw crushers, Raymond mills, and cyclones. Advanced milling technologies eliminate oversized particles.

Physical Properties

Key properties for talc include composition, color, particle size, water solubility, and oil absorption. Some grades are available with an average particle size of 1 to 3 μm, but most are around 5 to 15 μm. Brightness ranges from 70 to 85 for inexpensive grades and 87 to 92 for premium grades. Oil absorption depends on particle shape and size but in general fits in between calcium carbonate and kaolin. Slurry pH is basic at 9 to 10. Talcs are hydrophobic and organophilic [7].

Coatings Performance

Talcs are used in many different types of coatings including interior and exterior trade sales paints, primers, traffic paints, and industrial coatings. Western platy talcs develop good flatting and provide good chemical and water resistance due to high-purity and low-soluble calcium. These are best for sanding primers because of softness and good sealing properties, while coarse grades help develop surface roughness ("tooth"). Platy talcs have good flow properties and improve barrier resistance and durability in exterior trade sales paints and enamel hold-out in interior applications. Talcs also enhance durability of traffic paints. Eastern acicular talcs have better color and develop lower viscosity at high loadings due to lower oil absorption.

SILICA

Description

Silica is a general term describing products with the chemical formula SiO_2 of which both natural and synthetic types are available. Those most widely used in paint and coatings are crystalline, microcrystalline, diatomaceous, precipitated, and fumed. They differ in method of production, physical properties, and function.

Crystalline silica is produced by crushing, grinding, and classifying quartz. Microcrystalline differs from crystalline in that its deposits, found principally in Arkansas, have a higher concentration of fine particles. It is produced in a similar manner as crystalline, but the ore is finer in particle size. Both are decreasing in usage because of reported health and safety issues related to crystalline silica.

Diatomaceous silica, also known as diatomaceous earth or simply diatomite, consists of the skeletal remains of single-celled aquatic plants called diatoms. Domestic deposits are located in California, Nevada, and Washington. The ore is crushed, milled, dried, and air-classified. Calcined grades are processed in high-temperature rotary kilns and separated into selected particle size ranges by air classification. These products have superior color and are preferred for coatings applications.

Synthetic silicas are produced by a number of differing chemical and thermal processes. Precipitated silica is produced by acidification of sodium silicate to form aggregates of ultra-fine particles. Aggregate size and degree of structuring are controlled by reaction conditions. Fumed silica, produced via high temperature hydrolysis of silicon tetrachloride with hydrogen, also exists in aggregates of ultra-fine particles, and particle size and surface area are also dependent on reaction conditions.

Physical Properties

Since processing of crystalline silica is essentially a size reduction operation, particle size and particle-size distribution are the primary means of differentiating products. Crystalline silicas range from 2 to 10-μm average particle size. Microcrystalline grades are easier to disperse and are less abrasive than crystalline grades. Brightness is from 85 to 90% and pH from 6 to 7. Oil absorption is intermediate between calcium carbonate and hydrous kaolins. These extenders ae translucent and don't contribute to hiding as do some calcium carbonates and kaolin. Diatomaceous silica is a very high oil absorption material found in aggregates ranging in mean particle size of 2 to 20 μm. Calcined grades have a brightness of 87 to 90%.

The synthetic silicas are differentiated by surface area and particle size. Surface area of precipitated types is about 60 to 300 m^2/g, while fumed silica ranges from 50 to 400 m^2/g. Ultimate particle size of the individual particles are less than 0.1 μm for both; however, precipitated may develop larger aggregates. Fumed silica has a pH of 3 to 4, and precipitated is 6 to 8. These grades are often made hydrophobic by reaction with organofunctional silanes to improve performance in coatings.

Coatings Performance

Crystalline silica is used in trade sales, industrial coatings, and primers. It is an inexpensive extender which contributes to low sheen control, burnish resistance, and durability with minimal impact on rheology in latex trade sales paints. It is also used in powder coatings where its low binder demand does not affect flow properties.

Diatomaceous silica is primarily used as an inexpensive flatting agent in latex trade sales paints because of its high binder demand [*8*]. Precipitated silicas are used as flatting agents in solvent-based industrial coatings. Fumed grades, more expensive than precipitated because of high-energy requirements during production, are used as rheology modifiers and flatting agents in industrial coatings.

MICA

Description

Mica is a family of hydrous aluminum potassium silicates of which one, muscovite, has the chemical formula $K_2O{\cdot}3Al_2O_3{\cdot}6SiO_2{\cdot}2H_2O$. Micas are best known for a very platy particle shape and high aspect ratio. These are coarser in particle size than most extenders. Higher-aspect-ratio micas are produced by frictional wet grinding. Dry processing in high-pressure air jets to both delaminate and reduce the particles results in lower-aspect-ratio mica.

Physical Properties

Most coating grades of mica have an average particle size of 5 to 50 μm. Residue of 325 mesh varies from less than 1 to as high as 50%, depending on the particle size of the product. Brightness ranges from 65 to 80%, low compared to other extenders, while pH is 7 to 8. Oil absorption is higher than other hydrous minerals and is closer to coarse calcined kaolins.

Coatings Performance

Mica is best known for its very platy particle shape, which forms layers parallel to the paint film. Mica reinforcement increases durability and resistance to moisture penetration, corrosion, checking, heat, and chemicals. It helps prevent cracking in exterior architectural coatings and traffic paint. It prevents cracking and sagging in textured coatings. Mica provides good barrier resistance in primers and roof coatings [*9*]. Its platy particle shape, however, limits loading levels due to rheology constraints.

BARIUM SULFATE

Description

Barium sulfate ($BaSO_4$) is available as barytes, its naturally occurring form, or as blanc fixe, a synthetic precipitate. Barytes has a nodular particle shape with deposits found predominantly in Nevada, Georgia, Missouri, Montana, Tennessee, Illinois, and Washington. The ore is beneficiated by flotation techniques and then wet ground to obtain the required particle size and bleached to improve color. Some higher quality ores are dry ground and air classified. Blanc fixe is a very white, fine-particle-size extender not as widely used in paints and coatings as barytes. It is precipitated to a specific particle size from solutions of barium salts and sodium sulfate. Blanc fixe is also used to make lithopone (extended) grades of pigments. Multistage washing and filtration removes soluble impurities, and the products are then dried and ground.

Physical Properties

Barytes is best known for its high density and very low oil absorption relative to other extenders. Particle size ranges from about 1 to more than 10 μm depending on the grade. Brightness also varies from below 70 to greater than 90% depending on the source and degree of beneficiation. Slurry pH runs from 4 to 10. Blanc fixe is a more uniform product with a 1 to 2-μm average particle size and high brightness (95 to 98%).

Coatings Performance

Barytes is used in industrial and automotive primers and undercoats. Its low oil absorption allows for high loadings with less impact on rheology compared to higher binder demand extenders. It helps develop a smooth surface with minimal impact on the gloss of subsequent coats. Because extenders are sold by weight, its high density can be a disadvantage in trade sales coatings where more weight is needed to fill a given volume. Higher density relative to other pigments can increase settling and cause stability problems. Blanc fixe has been used to develop dry hiding as a partial replacement for titanium dioxide in trade sales and industrial coatings [*10*].

OTHER

Wollastonite

Wollastonite is a calcium metasilicate with the chemical formula $CaO{\cdot}SiO_2$ of which the primary domestic sources are New York and California. It has an acicular particle shape and is brown to white in color. It is principally produced by dry processing. Typical coating grades range from 2 to 10 μm in mean particle size. Brightness ranges from 80 to 95%, and pH is 9 to 10. Its acicular particle shape provides some reinforcement in coatings, and high pH is effective in buffering latex systems. Surface-modified grades improve performance in industrial coatings by both reducing resin demand and improving bonding between the mineral and resin [*11*].

Nepheline Syenite

Nepheline Syenite is an anhydrous sodium potassium aluminum silicate with the chemical formula $K_2O{\cdot}3Na_2O{\cdot}4.5Al_2O_3{\cdot}20SiO_2$ and is mined and beneficiated in Canada. It has high brightness (95 to 98%) and is relatively coarse in particle size (2 to 16 μm). Its low binder demand makes it particularly effective in exterior trade sales architectural coatings. Nepheline syenite provides good tint retention and prevents checking and cracking in exterior paints and also develops good scrub resistance in interior latex paints.

Sodium Aluminosilicates

Synthetic sodium aluminosilicates are produced by reacting aluminum sulfate with sodium silicate to produce a structured extender. These have high brightness (92 to 98%) and relatively coarse particle size of 5 to 6 μm. Sodium aluminosilicates are used as partial replacements for titanium dioxide in latex trade sales paints similar to calcined kaolin but at higher cost; some of the highly structured grades are used as flatting agents in latex paint.

Alumina Trihydrate

Alumina trihydrate (ATH) has the chemical structure $Al(OH)_3$ and is produced from bauxite ore as an intermediate in aluminum production. It is most commonly used as a flame retardant and smoke suppressant in thermoplastic and thermoset polymer applications. ATH has a brightness ranging from 85 to 98% depending on the grade. Some very fine particle size grades, less than 1 μm, may be effective in spacing titanium dioxide in trade sales paints.

COMPARISON OF DIFFERENT EXTENDER PIGMENTS

Physical Properties

Physical properties of the pigment extenders described above are compared in Tables 1 and 2. Calcium carbonates are available in different particle size grades and are very white in color and high in brightness. Low oil absorption enables high loading levels with minimal influence on rheology. High pH makes these products appropriate for latex paints. Surface-treated grades are available for solvent-based systems. Precipitated forms are higher in brightness, finer in particle size, and have higher oil absorption approaching that of calcined kaolins.

TABLE 1—Physical properties of pigment extenders.

	Ground Calcium Carbonate	Precipitated Calcium Carbonate	Hydrous Kaolin	Calcined Kaolin	Talc	Crystalline Silica	Mica
Free moisture, %	0.5	0.5	1.0	0.5	0.2–.5	0.3	0.5
Specific gravity	2.71	2.71	2.58	2.63	2.8	2.65	2.82
Brightness, %							
Fine	90–95	97–98	88–90	90–95	75–92	85–90	...
Coarse	85–90	...	85–88	...	70–92	85–90	65–80
Ave particle size							
Fine, μm	1–3	0.5–1.5	0.2–5	0.8–2.5	1–3	2–3	...
Coarse, μm	5–12	...	...	...	5–15	5–10	5–50
pH	9.5	9–10	4–7	4–5	9–10	6–7	7–8
+325 Residue, %	0.01–1	<0.05	0.01–.1	0.01	0.01–1	<1–4	1–50
Oil absorption, g/100 g	10–20	30–60	30–50	50–100	25–55	20–30	60–65

TABLE 2—Physical properties of pigment extenders.

	Diatomaceous Silica	Precipitated Silica	Fumed Silica	Barytes	Wollastonite	Sodium Alumino-Silicate	Nepheline Syenite
Free moisture, %	<1	<1.5	5	<1	<1	<1	<1
Specific gravity	2.30	2.20	2.20	4.40	2.90	2.1–2.3	2.60
Brightness, %	87–90	96	white	80–95	80–95	92–98	95–98
Ave. particle size							
Fine, μm	3–4	0.01–0.05	0.01–0.05	1–4	2–4	...	2–4
Coarse, μm	5–10	...	...	8–12	7–10	5–6	7–16
pH	9–10	6–8	3–4	4–10	9–10	7–10	10
+325 Residue, %	<1–3	0.01	0.01	<1	<0.1	<0.5	<0.5–6
Oil absorption, g oil/100 g	90–130	100–300	100–400	10–15	20–40	75–115	20–30

TABLE 3—Comparative properties of extender pigments in coatings.

	Calcium Carbonate, 5 μm	Hydrous Kaolin, 0.5 μm	Hydrous Kaolin, 4.8 μm	Calcined Kaolin, 1.8 μm	Talc, 8 μm	Silica, 5 & 10 μm
Hiding contribution	Very low	Very high	Moderate	Very high	Moderate	Moderate
Gloss	Low	Moderate	Low	Low	Low	Low
Enamel holdout	Poor	Excellent	Very good	Poor	Fair	Poor
Stain removal	Poor	Excellent	Very good	Poor	Fair	Fair
Abrasion resistance	Fair	Poor	Poor	Excellent	Good	Good
Adhesion	Poor	Very good	Very good	Fair	Good	Very good
Water spot resistance	Poor	Excellent	Excellent	Excellent	Good	Excellent
Chemical resistance	Very poor	Very good	Very good	Good	Good	Excellent
Viscosity	Very low	High	Low	High	High-mod.	Low
Stability	Poor-very good	Excellent	Excellent	Very good	Poor-very good	Excellent
Suspension	Poor	Excellent	Very good	Very good	Very good	Poor
Ease of brushing	Fair	Excellent	Excellent	Good	Fair-poor	Good
Leveling	Excellent	Very good	Very good	Good	Fair	Very good

TABLE 4—ASTM Test Methods for extender pigments.

Standard	Title
Specifications	
D 602-81	Standard Specification for Barium Sulfate
D 603-66	Standard Specification for Aluminum Silicate Pigment (Hydrous)
D 604-81	Standard Specification for Diatomaceous Silica
D 605-82	Standard Specification for Magnesium Silicate (Talc)
D 607-82	Standard Specification for Wet Ground Mica
D 1199-86	Standard Specification for Calcium Carbonate
D 3619-77	Standard Specification for Aluminum Silicate Pigment (Anhydrous)
Analytical	
D 715-86	Analysis of Barium Sulfate Pigment
D 716-86	Evaluating Mica Pigment
D 717-86	Analysis of Magnesium Silicate Pigment
D 718-86	Analysis of Aluminum Silicate Pigment
D 719-86	Analysis of Diatomaceous Silica Pigment
Physical Properties	
E 70-90	pH of Aqueous Solutions with the Glass Electrode
D 153-84	Specific Gravity of Pigments
D 281-84	Oil Absorption of Pigments by Spatula Rub-out
D 1210-79	Fineness of Dispersion of Pigment-Vehicle Systems
D 1366-86	Reporting Particle Size Characteristics of Pigments (Practice)
D 1483-84	Oil Absorption of Pigments by Gardner-Coleman Method
D 2448-85	Water-soluble Salts in Pigments by Measuring the Specific Resistance of the Leachate of the Pigment
D 3360-80	Particle Size Distribution of Common White Extender Pigments
D 4139-82	Determining Volatile and Non-volatile Content of Pigments (Guide)

Hydrous kaolins are the finest particle size naturally occurring extenders. Neutral predispersed grades are available for latex systems, and acid grades are available for solvent-based systems. These products have very low residue, which improves gloss development. The calcined grades have slightly better color, and higher oil absorption contributes to opacity.

Talcs are available in a wide variety of grades depending on the source. These are more similar to calcium carbonate in particle size, although brightness is somewhat deficient. Platy particle shape is a key parameter. Crystalline silica has lower binder demand than kaolin or talc. Coarser grades are effective flatting agents. Mica is much coarser in particle size than most extenders. It also has lower brightness and high residue, which limit the levels at which it may be used.

The high oil absorption of diatomaceous earth makes it an effective flatting agent. Precipitated and fumed silica, as more carefully controlled reaction products, are more appropriate for industrial coatings applications. Barytes, wollastonite, and nepheline syenite are coarser particle-size products which are less broadly used than finer particle-size extenders.

Comparative Performance in Coatings

Performance characteristics of the extenders previously discussed are compared in Table 3. Coarse calcium carbonate filler does not provide significant improvement in coatings performance and is primarily used to reduce cost. Fine-particle-size hydrous kaolin helps develop hiding power and gloss. These extenders develop good film properties, help maintain stability, and aid in coating application. Calcined kaolin also contributes to opacity development and is fairly good in maintaining film properties, rheology, and application properties. Talc develops good film properties but may have an deleterious effect on rheology, particularly at higher loadings. Coarse amorphous silica is an adequate filler.

PERTINENT ASTM TEST STANDARDS

ASTM standards useful in evaluating extender pigments are shown in Table 4. Standard specifications are useful for categorizing extenders by mineral type and provide some general test guidelines. Analytical standards are useful for chemical analysis of extenders for identification purposes.

Standards for measurement of physical properties are very useful in categorizing extenders and for predicting suitability for a particular coatings application. Particle size, oil absorption, fineness of dispersion, pH, and water-soluble salt content are important parameters in determining the suitability of an extender for a particular coatings application. Actual product specifications should always be mutually agreed upon by supplier and user.

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25

Metallic Pigments

by Russell L. Ferguson[1]

METALLIC PIGMENTS, INCLUDING ALUMINUM, zinc, gold, bronze, nickel, and stainless steel, provide the paint and coatings industry with a variety of aesthetic and functional properties. These pigments, either in flake or powder form, contribute to the metallic effects associated with automotive topcoats; general industrial finishes; silver, gold, and copper finishes; metallic ink systems; and many of the high-performance primers for coatings systems. In addition to providing metallic and polychromatic effects, they provide functional, anticorrosive benefits.

History and Manufacturing Methods

The origin of metallic coatings can be traced back to early civilizations, who utilized thin, gold sheets to overlay wood, bone, or other materials. As the artisans molded these foil sheets, the thin edges would break off into flakes. It was soon discovered that by mixing these flakes in a resinous polymeric material, a similar effect could be achieved. This process was later continued, and by shredding the foil into flakes, artisans were able to produce gold and later silver and bronze metallic effects on ornamental objects. In the middle of the 19th century, a mechanical stamping process, along with newly developed smelting processes, made gold and silver substitutes more readily available. Aluminum, gold, bronze, and later stainless steel and nickel became readily accepted substitutes.

Today, with the exception of zinc powder, most metallic pigments utilize the Hall Wet-Ball Milling Method [*1*]. This process carries out the particle-size reduction in the presence of a suitable lubricant and solvent, offering a safer production method. Eliminating the explosive hazards associated with mechanical stamping processes has allowed the production of finer metallic flakes that find widespread use today. Stamping and dry-ball milling are still utilized in the manufacture of gold bronze flakes.

The post-milling manufacture processes for metallic flakes generally include a screening operation to remove undesirable particles, along with tight controls on aesthetic properties. Color adjustments, along with polishing and blending operations, are utilized in the final stages of the manufacturing process. The metallic flake pigments are available as a dry flake or in a wide range of solvents, including aliphatic and aromatic solvents, alcohols, plasticizers, water, and coalescing solvents.

Zinc powders have a similar, but divergent, history. Not being sought after for aesthetic properties, they were first used in the mid-1800s for anticorrosive functionality and were referred to as "blue powder." Zinc-gray coatings were used extensively for industrial and marine environments by the early 1900s. However, it was not until the late 1930s and 1940s that the industry gained a firm foothold. The manufacture of zinc dust is carried out by melting and vaporizing zinc metal followed by a controlled condensation of the vapor in an inert atmosphere. The product is collected, screened, classified, and packaged [*2*].

Properties

Metallic pigments share similar properties; however, each is distinct enough to be considered separately.

Aluminum

Aluminum pigments are manufactured from aluminum metal with a purity ranging from 99.3 to 99.97%, depending on the grade being manufactured. Although amphoteric in nature, the pigment exhibits a high degree of chemical resistance. Aluminum pigments owe their aesthetic and functional properties to the geometry of the particle, particle-size, and particle distribution. The pigment is a flake-like particle (lamellar) and has either a round or irregular perimeter. Once formulated into a coating, they orient parallel to the substrate and film surface. This orientation provides for exceptional barrier properties in the appropriate coating system. Metallic or polychromatic coatings containing aluminum flake pigments, either by themselves or in combination with transparent colors, offer a two-tone quality often sought after. The two-tone, or flop, feature is an important characteristic in many automotive top coats.

There are two general types of aluminum pigment: leafing and nonleafing. Leafing grades are manufactured using a saturated fatty acid as the lubricant (typically stearic acid), which allows the flakes to float at, or near, the surface of a paint film. This continuous layer of flakes provides a solid silver color, unable to be tinted with other pigments. The nonleafing grades utilize an unsaturated fatty acid as the lubricant (typically oleic acid) which allows the flakes to orient throughout the paint film. Nonleafing pigmented coatings can be tinted with organic pigments to offer a polychromatic appearance.

Aluminum flakes range in size from 0.1 to 2.0 μm in thickness, and 0.5 to 200 μm in diameter. Generally, aluminum flakes are supplied in a paste form with a typical composition

[1]Vice President of Technical Functions, Silberline Manufacturing Co., Inc., R.D. 2, P.O. Box B, Tamaqua, PA 18252.

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of 64% aluminum metal, 1% lubricant, and 35% hydrocarbon solvent [3].

Gold Bronze

Gold bronze pigments are neither gold nor bronze, but are typically manufactured from a composition of copper and zinc alloy. By altering the copper-zinc ratios, four standard gold bronze colors can be produced. The standard alloy subdivisions are: (1) copper—100% copper, 0% zinc; (2) pale gold—90% copper, 10% zinc; (3) rich pale gold—85% copper, 15% zinc; and (4) rich gold—70% copper, 30% zinc. Further oxidative treatments can be utilized to produce special colored bronzes, varying from brown-golds to oranges and reds. Additionally, blending of any of the above-mentioned bronze powders will result in an almost unlimited pallet of gold-bronze colors.

Gold-bronze pigments are flake-like particles (lamellar) with an irregular perimeter. In a coating or ink application, they orient parallel to the substrate and film surface [4].

Zinc Pigment

Zinc dust is the only metallic pigment that is not found in a lamellar form. Produced through the condensation of zinc vapor in an inert atmosphere, the zinc dust is a spherical particle averaging about 8 μm in diameter. Zinc dust is predominantly zinc metal (96 to 97%), with some zinc oxide (3 to 4%), and traces of lead, cadmium, iron, and other elements.

Stainless Steel Flake

Stainless steel is a composition of iron, chromium, nickel, manganese, and molybdenum. There are three groups of stainless steel alloys available: (1) martensitic, (2) ferritic, and (3) austenitic, differentiated according to alloy composition. Of the three groups, austenitic is the most corrosion resistant and typically used to manufacture stainless steel flake. Austenitic alloys owe their corrosion resistance to higher levels of nickel and molybdenum. Stainless steel pigment has a lamellar geometry and will orient itself parallel in a coating system. Stainless steel flake has a high degree of durability and will resist tarnishing, abrasion, and chemical attack. Additionally, stainless steel flake is able to maintain stability in water-based systems.

Nickel

Nickel pigments can be found in either powder or flake-like form. They are typically composed of nickel metal, with traces of carbon, oxygen, sulfur, and iron. Nickel flake powders are available dry, as a paste in mineral spirits, or as a paste in mineral oil. Nickel powders have good electrical conductivity [5].

METALLIC PIGMENT GRADE CLASSIFICATION

Aluminum Pigments

Aluminum pigments are more widely used than any other metallic pigment and can be divided into a number of different categories. The grade classification is, in general, determined by the intended use. Most of the following categories contain a wide range of grades from very coarse, large flakes to very fine, small flakes.

Leafing Grades

The standard grade category is composed of a series of grades from very coarse flakes (having water coverage from 6000 to 9000 cm^2/g) to very fine flakes (having water coverage in the area of 35 000 cm^2/g). These grades are used, primarily, in trade sales and maintenance coatings. Their leafing values are traditionally 50% minimum.

The ultra-leafing grades are characterized by very high leafing values (in the area of 90 + %) and exceptional brightness. Their uses include aerosol coatings and ink applications.

Nonleafing Grades

The standard grades are represented by a full range of products from very coarse, low-opacity to very fine, high-opacity grades. They are used in diverse applications from maintenance coatings to general industrial applications and automotive refinish.

The automotive grades are distinguished from standard grades by possessing improved aesthetics, including brighter, more sparkling appearances, with tighter control on particle-size distribution. Many subcategories exist under this heading, including specialized grades for base coat/clear coat systems, circulation resistance, etc.

Plasticized and polymer-modified grades are represented by a full range of products designed for end-use systems that cannot tolerate solvents (mineral spirits). The primary end use is plastic and ink applications.

The dedusted grade category comprises dry aluminum flakes held loosely together by Teflon bonds, resulting in a nondusting product. These grades are used in some general industrial coatings; however, the primary application is to act as a sensitizer for slurry explosives.

The surface-treated grades include aluminum flakes whose surface chemistry has been altered to allow for improved aluminum flake performance. These grades are used in powder coatings and some solvent-borne coatings where improvements in flake orientation and performance are desired.

The aqueous grade category consists of aluminum pigments treated with various chemical components to stabilize the flake for use in waterborne systems. Various levels of inhibition and performance are available.

Gold Bronze Pigments

These pigments are primarily used for coating and ink applications. They can be divided into four categories, based on alloy composition:

1. *Copper*—coppery-red color (100% copper).
2. *Pale Gold*—reddish gold color (90% copper; 10% zinc).
3. *Rich Pale Gold*—gold color (85% copper; 15% zinc).
4. *Rich Gold*—greenish gold color (70% copper; 30% zinc).

Zinc Pigment

The zinc pigment, dust and flake, is used in coatings, primarily for corrosion-resistant properties. The categories available are:

1. *Regular Zinc Dust*—7 to 8-μm particle-size diameter.
2. *Fine Zinc Dust*—5 to 6-μm particle-size diameter.

3. *Ultra-Fine Zinc Dust*—3 to 4-μm particle-size diameter.
4. *Zinc Flake*—Available in several grades, based on particle-size.

Stainless Steel Flakes

These flakes are used in specialized coatings that require good resistance to severe environmental conditions.

Nickel Powder and Flake

The powder and flake are used in coating and plastic systems to provide electrical conductivity and corrosion-resistance characteristics.

FORMULATION AND APPLICATION GUIDELINES

Formulation Considerations

Metallic flake pigments, by the nature of their geometry and composition, are malleable and therefore somewhat fragile. The dispersion of these flakes into a coating system is critical in maintaining optimum aesthetic and functional performance. The preferred dispersion process involves the addition of vehicle or solvent to the metallic pigments, with slow-speed mixing, to gently separate the flakes. Once a thick, uniform slurry of metallic flakes, solvent, and vehicle is achieved, the formulator can continue to let down to final product composition. Severe dispersion techniques such as Cowles high-speed mixers, sand mills, etc. will destroy the flake integrity, resulting in loss of aesthetic and perhaps functional properties. Zinc pigment, which is not a flake, can be dispersed using conventional paint dispersion techniques.

Appropriate selection of vehicle, solvents, and additives must also be considered when formulating with metallic pigments. The leafing properties of aluminum and bronze flakes can be detrimentally affected by such properties as acid value of the resin; polar solvents, or solvents with low-surface tension; moisture in the system; and additives, including driers that are good wetting agents. Since most metallic pigments contain mineral spirits, coating system compatibility must be considered.

The current trend toward waterborne coatings also poses problems in formulation. Dispersion of metallic pigments can be accomplished through the correct selection of an appropriate coalescing solvent. However, even good dispersion will not guarantee good coating performance. Metallic waterborne coatings have the potential for hydrogen gas generation. This potential has been addressed by many manufacturers through various inhibiting processes. While many inhibited grades are available on the market today, performance may vary in different aqueous systems. In addition to the potential for hydrogen gas generation, tarnishing and printability have been addressed by manufacturers of gold bronze flakes. Stainless steel flakes, because of the very nature of their composition, can be used in waterborne coating formulations without the possibility of gas generation.

Another solution to the VOC (volatile organic compound) problem is the use of powder coating systems. Specialized grades of aluminum pigments have been developed to meet the needs of these 100% solids systems. These grades have been surface-treated to allow for improved flake orientation, along with modified electrical conductivity. Applied electrostatically, the surface-treated aluminum flake will perform in a similar fashion to the powder coating resin.

The application of metallic pigmented coatings and inks will depend on the system being used. Traditional ink application methods will apply to both leafing and nonleafing metallic pigments. In the case of coating systems, leafing metallic pigments can be applied by brush, roller, or spray application. Nonleafing grades, however, must be applied using appropriate spray application techniques. Improper application techniques can lead to poor flake orientation which will result in reduced aesthetic and functional properties.

Market Applications

Metallic pigments are widely used in the coating, ink, plastic, and explosive markets. In the coating industry, metallic pigments offer both functional and aesthetic properties. Those pigments that are lamellar (aluminum, gold bronze, stainless steel, and nickel) are opaque and orient parallel to substrate and coating film surface. Thus, they provide a barrier to ultraviolet (UV) and infrared (IR) light, along with moisture and oxygen penetration. Zinc pigment, while not a flake, possesses superior corrosion protective properties for steel or iron substrates. Because zinc is higher in the electromotive series, it acts as the anode of a corrosion cell. The iron or steel substrate is protected by the zinc because of the formation of insoluble compounds with lower oxidation states.

The aesthetic benefits of metallic pigments are widely known in the coatings industry. In the area of trade sales and maintenance coatings, aluminum pigments provide very bright, silvery finishes typically found in many roof coatings, aerosol applications, and bridges. In general industrial and automotive coatings, various polychromatic and metallescent appearances are produced utilizing nonleafing grades.

In the ink and plastic industries, the primary benefits derived are from aesthetic properties. Gold bronze flakes, along with aluminum flakes, provide attractive polychromatic finishes.

The explosives industry utilizes aluminum flake pigment as a sensitizer in slurry explosives.

Economics of Use

The extensive markets for metallic pigments has mandated their use in a wide range of systems for many years. Their properties, both functional and aesthetic, along with the traditional economic values associated with their properties, have established them as an important raw material in the coating, ink, and plastic markets. The economics of these pigments are dependent on a number of factors, including cost of the raw material, degree of sophistication of the pigment, and the end product for which it is intended.

TESTING

ASTM Test Methods

ASTM covers various specifications and test procedures for metallic pigments. Included are:

- D 962-81—Specification for Aluminum Pigments, Powder and Paste, for Paints
- D 480-88—Test Method for Sampling and Testing of Flaked Aluminum Powders and Pastes (includes tests for volatile analysis; coarse particles; leafing properties; brushing, smoothness, lustre properties; and easily extracted fatty materials)
- D 95-83—Test Method for Water in Petroleum Products and Bituminous Materials by Distillation
- D 185-84—Test Methods for Coarse Particles in Pigments, Pastes, and Paints
- D 235-87—Specifications for Mineral Spirits (Petroleum Spirits) (Hydrocarbon Drycleaning Solvent)
- D 267-82—Specifications for Gold Bronze Powder
- D 520-84—Specification for Zinc Dust Pigment
- D 521-81—Test Methods for Chemical Analysis of Zinc Dust (Metallic Zinc Powder)
- D 4017-88—Test Method for Water in Paints and Paint Materials by Karl Fischer Method

Test Methods Not Covered by ASTM Specifications

ASTM test methods cover many of the properties of metallic pigments; however, there are additional tests which further serve to characterize these pigments. Included are:

Acid Spot Test

This test is designed to determine the acid resistance of aluminum pigments in coating systems. A metallic pigmented coating is tested by placing drops of a 10% solution of hydrochloric acid on the panel. Three rows of three drops are placed on the panel and each row is removed after 1-h intervals (Fig. 1). If the aluminum pigment is acid resistant, no spotting will be apparent after the first or second hour, with only slight spotting after 3 h. A nonacid-resistant aluminum will show definite spotting from the acid solution after the first hour.

Particle-Size Analysis

One of the key elements in any metallic pigment is the particle-size distribution. Instruments are available on the market today to characterize, or fingerprint, metallic pigments. Unfortunately, most of these instruments are incapable of characterizing lamellar-shaped pigments; however, their increased sophistication has allowed for a very close approximation. In addition to providing a distribution of the particles in a pigment, also provided are surface area, average particle size, and percentages at various levels.

Water Coverage

This test can be used to determine the particle-size thickness and surface area of leafing and nonleafing metallic flake pigments. This test has been fully described by Edwards and Ray [*6*]. A dry, metallic pigment is dusted onto a surface of clean, distilled water, which is contained in a shallow, rectangular pan. The accurately weighed flake metallic pigment is dusted onto the surface of the water and separated until it is one flake thick. The coverage of metallic flake on the water

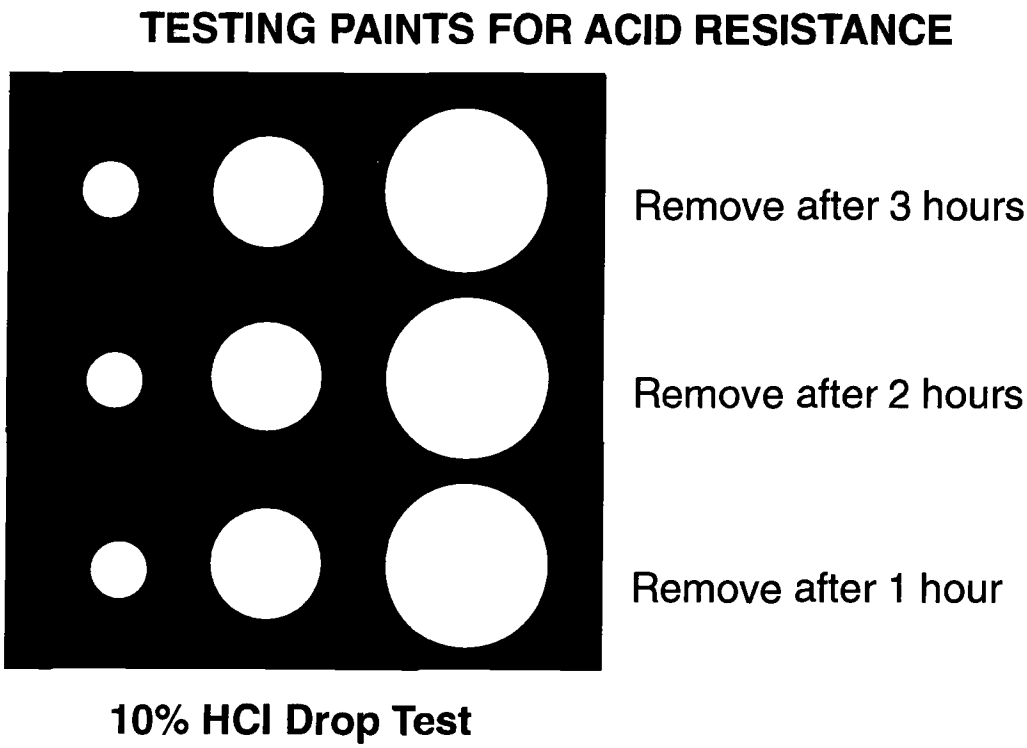

FIG. 1—Testing paints for acid resistance.

can then be measured, and total surface area can be calculated based on the weight of the metallic flake pigment used. The thickness of the metallic flake pigment can also be calculated using simple density and volume calculations.

Degradation Test

This test is designed to determine the level of flake deterioration in a coating system when subjected to severe stress. Automotive coating systems are often circulated through pumps, regulators, and long piping and tank systems to keep all the components of the coating in suspension. Circulation may have detrimental effects on the metallic flake integrity, causing bending, curling, and even breakage of the metallic flake. The loss in aesthetic properties due to flake deformation results in a darkening of the coating, along with a change in the flop characteristic. This test is designed to evaluate the capability of the metallic flake to resist deformation under these stress conditions.

A metallic pigmented coating is placed into a water-jacketed Waring blender. Using a standard cutting blade, the blender is operated at high speeds for 5 to 15 min. The metallic coating is a sprayed pre- and post-blender operation, and visual and instrumental comparisons are made. The degree of flake deformation can be translated into numerical data based on the brightness of the metallic coating (face and flop).

Gassing Test

Aluminum and other metallic pigments, by their very nature, will react with water to generate hydrogen gas. Today, due to VOC regulations, more and more coating and ink systems are moving toward waterborne technologies. Metallic pigment manufacturers have developed technologies to inhibit the aluminum flake pigments, and this test is designed to determine the gas generation potential and stability characteristics of metallic flake pigmented aqueous coating systems. Approximately 200 mL/s of a metallic pigmented coating is charged into an Erlenmeyer flask. Attached to the flask is a glass condenser with Tygon tubing coming out of the top and extending into an inverted buret filled with water. The Erlenmeyer flask is suspended in a hot oil bath, which accelerates the potential for hydrogen gas evolution. This test is operated for seven days (168 h) at a temperature of 52°C. The acceleration of the environmental conditions will allow for hydrogen gas generation, which will pass out of the Erlenmeyer flask, through the Tygon tubing, and into the inverted buret. The water in the inverted buret is displaced by the hydrogen gas and generation can be easily read through this displacement (Fig. 2). The specifications for gas generation should be designed around the metallic flake pigment and coating system tested. The specification for gas generation should not exceed the volume of the buret (typically, 100 mL/s).

Electrical Resistivity/Conductivity

In waterborne coating systems it is often useful to know the conductivity or resistivity of the components of the system. In order to measure metallic pigments, it is necessary to disperse the metallic pigment in an isopropyl alcohol/deionized water mixture. This mixture should be agitated using an air mixer for at least 5 min, after which the metallic pigment should be filtered out. The resultant filtrate can be tested for resistivity/conductivity using a conductivity meter (i.e., Jenway Conductivity Meter, Model 4010).

pH Measurement

In waterborne coatings and ink systems, it is often necessary to know the pH of the components of the system. The pH

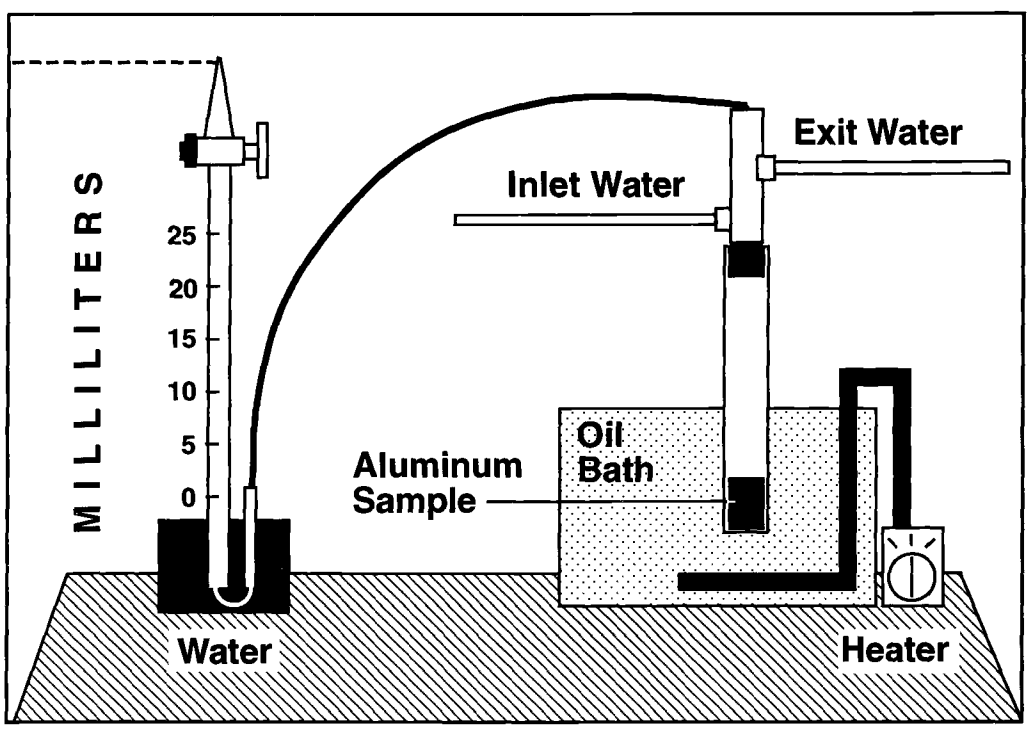

FIG. 2–Gas evolution test for metallic coatings.

of metallic pigments can be evaluated by adding the metallic pigment to a mixture of isopropyl alcohol/deionized water. The slurry should be mixed using an air mixer for at least 5 min. The metallic pigment should then be filtered out, and the pH of the resultant filtrate can then be evaluated.

Aesthetic Properties

Metallic pigments are used for the aesthetic properties they lend to coating systems. Each metallic pigment grade offers a slightly different appearance property to these coatings, and it is necessary to be able to assess these differences. Visual and quantitative data can be generated based on a number of these properties. Four of the most important properties are:

- The *face-color*, or *head-on-brightness*, attribute generally refers to the amount of reflected light from a metallic pigmented coating when viewed at approximately 20 to 25° off of specular.
- The *flop, flip/flop,* or *metallic travel angle* refers to the amount of reflected light when viewing a metallic pigmented coating at an angle that is 70 to 110° off of specular. Metallic travel is often referred to as the degree in change of brightness going from the face angle to the flop angle.
- *Seed level* refers to the degree of protrusion of the metallic flake through a coating film surface.
- *DOI (distinctness of image)*, closely related to gloss, refers to the reflection of an image from a metallic pigmented coating back to the observer. The clearer, or more distinct, the reflected image, the higher the DOI value. Typically, the finer the pigment, the higher the level of DOI.
- *Patina* is the packing appearance of the metallic flakes in coating systems. A good patina is often described as having a smooth, velvety appearance, lacking individual flake identity in the coating. If an observer sees only a continuous metallic film without breaks, protrusion, or individual flake identity, the metallic coating is considered to have a good patina. Many coating systems and pigment parameters affect the patina of a coating system. Typically, higher solids coatings, poor application methods, coarse pigments, and poor flake orientation contribute to poorer patina properties.
- The *color* attributes from the face and flop angles can be numerically measured. There are a number of instruments available today that are capable of measuring reflected light at different angles. All of them are goniospectrophotometers and are capable of measuring reflected light on metallic pigmented coatings at angles from 10° off specular to 110° off specular. ASTM Task Force Committee E-12.03.02 is currently working on a standard test method to evaluate metallic pigmented coatings utilizing specified goniospectrophotometric angles.

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26

Pearlescent Pigments

by Carl J. Rieger[1]

PEARLESCENT PIGMENTS, SOMETIMES REFERRED TO as nacreous pigments, are attempts to create the natural pearl luster effects seen in pearls or sea shells [*1*]. These pigments are high-refractive-index coatings on thin transparent flakes. The high-refractive-index material reflects incident light, and the transparent flakes allow some light to be transmitted through the flakes. Many different grades and types of pearlescent pigments are available. These grades range from materials for soft, satin-like effects from small-particle-size pigments to materials with sparkle metallic effects from larger-size pigments. A special type of pearlescent pigment that produces an iridescent color effect is termed an "interference pigment." These are very thin films with a high refractive index that exhibit color through an optical effect called light interference. This is similar to the "rainbow effect" seen in soap bubbles or in oil and gasoline slicks [*2*].

Because of these optical effects, pearlescent pigments can exhibit color without conventional light-absorbing pigments present. The colors arise from light interference effects that will be described in more detail later. Other types of pearlescent pigments have conventional absorption colors added by either depositing these colorants onto the pearlescent-pigment surfaces or by mixing colorants with pearlescent pigments.

HISTORY

The earliest use of pearlescent pigments is credited to French rosary makers in the 17th and 18th centuries. They used the scales of fish to impart pearl effects to the glass beads used in making rosaries. The modern era of pearlescent pigments began in the late 1920s when scales of fish, namely herring, were used to make simulated pearls for costume jewelry. Because "natural pearl essence," as the material extracted from the fish scales came to be called, was so expensive, synthetic pearl pigments were developed in the 1930s. These early synthetic pearl pigments were mainly lead salts. They possessed both the high refractive index and thin platelet shapes required for pearlescent pigments.

The modern commercial forms of pearlescent pigments consist of:

1. Titanium dioxide and ferric oxide coatings on mica.
2. Bismuth oxychloride crystals grown from a solution of bismuth salts.
3. Natural pearl essence, guanine, and hypoxanthane purines from fish scales.

Mainly because of its high cost, natural pearl essence is used in cosmetic applications such as fingernail polish, lotions, and creams.

Titanium-coated mica types of pigments evolved in the early 1960s through the work of Linton and others [*3–6*]. Coated mica of both the titanium dioxide and ferric oxide types have the dominant share of the pearlescent pigment market. This market involves uses in plastics, coatings, and inks in addition to cosmetic applications.

MANUFACTURING AND COMPOSITION

The type mica used in pearlescent pigments is called "wet-ground mica." This is ground as a water paste in Muller mills to give a delamination effect in the grinding process. As the mill rollers go over the mica, it becomes thinner and smaller in particle-size reducing aspect ratio. These mica flakes are then dried, sieved, and classified into the desired particle-size distribution.

Various particle sizes are available. The coarse particle-size distributions impart a sparkling, wet-look effect. The fine particle-size distributions impart a satin, soft appearance. The particle size for use in exterior grade pigments intended for automotive paints is very carefully controlled so that they contain no particles greater than 50 μm. This prevents clogging of paint filters in recirculation systems of automotive assembly plants and is vital for good application characteristics.

When titanium dioxide-coated types of pearlescent pigments are made, classified mica is suspended in water. Then, under controlled conditions of temperature and pH, titanium sulfate or titanium tetrachloride solutions are added slowly to yield uniform deposition of the hydrous titanium dioxide on the mica flakes or platelets. This suspension is filtered, dried, and calcined at temperatures above 800°C to convert the hydrous oxide into the crystalline form of titanium dioxide (TiO_2) and to increase its refractive index. The normal crystal form for these pigments is the anatase form of TiO_2, but conversion to the rutile form may be made by addition of small amounts of stannic chloride prior to the calcination operation. For the ferric oxide coated mica pigments, a similar procedure is followed except that ferric chloride solutions are added to the mica-water suspension instead of the titanium salts. By varying the thickness of the titanium dioxide

[1]Vice president, The Mearl Corporation, Applications and Development Laboratory, 3 Greentown Rd., Buchanan, NY 10511.

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or ferric oxide layer on the mica, the various interference colors can be obtained.

Bismuth oxychloride crystals are made by a precipitation process under controlled crystallization conditions. In this procedure, a bismuth nitrate solution in hydrochloric acid is added simultaneously with sodium hydroxide at a constant pH and temperature to grow flat, hexagonal-shaped platelets in the particle-size range of 11 to 15 μm. These are very high quality pearlescent pigments because of the narrow particle-size range, high refractive index, and flat shape of the bismuth oxychloride platelets. Bismuth oxychloride has about twice the reflectance of the best titanium dioxide-on-mica types of pearlescent pigments.

A lower quality and smaller size, 5 to 10 μm, type of bismuth oxychloride is made by a "dump" procedure in which a bismuth nitrate solution is added to a sodium chloride solution or vice versa. Because of the small size and irregular-shaped platelets obtained with this process, this type of bismuth oxychloride gives less luster on reflection than the 11 to 15-μm types.

Several patented post treatments [*7,8*] are available to modify commercial preparations and to give these pearlescent pigments the weathering resistance needed for exterior applications such as automotive paints, outdoor signs, and plastics.

OPTICAL PROPERTIES

Pearlescent luster is developed by the specular reflection of light as it strikes the broad surfaces of the platelets. These platelets are dispersed throughout the depth of the paint or ink film or plastic article. This reflection of light from pearlescent pigment particles dispersed throughout the thickness of the coating reinforces the luster and differentiates it from a strictly surface reflection as featured by leafing aluminum flake.

The requirements for a good pearlescent pigment are:

1. A high refractive index preferably greater than 2.
2. An optical thickness, i.e., the geometrical thickness of the layer multiplied by the refractive index, of approximately 100 to 140 nm for pearl (white) pigments. As interference pigments are produced by increasing the geometrical thickness, this optical thickness increases to 200 nm for gold, 250 nm for reds, 300 nm for blues, and 370 nm for green interference colors.
3. A high aspect ratio primarily derived from the mica. the larger the diameter-to-thickness ratio (the aspect ratio), the better the pearl effect. Another way of describing this would be to term it a "platey" structure. The mica itself plays no role in the optics and functions merely as a substrate upon which the high-refractive-index material is deposited.
4. Proper particle-size distributions are needed. Optimum luster occurs when the size distribution, measured by laser diffraction methods, falls between about 10 to 40 μm. Smaller particles, 5 to 10 μm, act as light scatterers and detract from luster. Particles larger than 40 μm give a grainy effect and reduce opacity. Pearlescent pigments are essentially transparent pigments and, as such, do not have good opacity or hiding.
5. Smooth surfaces that give high luster in comparison to rough surfaces that can cause light scattering. Uniformly dense surfaces also give low surface areas, as measured by the Brunauer-Emmett-Teller (BET) method,[2] that can improve weatherability.

APPLICATIONS

Industrial Coatings

Pearlescent pigments have been used in many industrial coating applications. One such use is coil coatings. Polymers often used in these applications, such as fluoropolymers, require high baking temperatures. Since they have been calcined at over 800°C during their manufacturing process, pearlescent pigments can tolerate high bake temperatures of 500 to 600°F (260 to 315°C) without any damage to pigment mechanical integrity or optical properties. Not all organic pigments can be used in such coil coating applications because of temperature limitations.

Pearlescent pigments find application in ink formulations such as gravure, silk screen, flexographic, and, to a lesser extent, offset printing inks. The particle size of some pearlescent pigments is too large for most offset applications.

Bismuth oxychloride pigments have been used for many years as coatings on wood furniture to sharply bring out the "grain" of the wood. Also, bismuth pigments have been utilized in the costume jewelry industry for coating and dipping beads and pearls.

Other applications for these pigments include roller and knife coating of leather and paper as well as coating of various types of toys and balls. The pigments are also used in the popular craft industry.

Automotive Coatings

Pearlescent pigments were first used in original-equipment-manufacture (OEM) automotive paint in the early 1980s, and they became a major styling tool about 1985 [*9,10*]. Since pearlescent pigments, chiefly the coated mica types, are transparent in nature, they do not "gray out" or "muddy up" the expensive transparent organic coating colorants used in automotive coatings. These pigments add to the chromatic effect of organic pigments and contribute to the "flop" or polychromatic effect desired in these coatings. Flop is defined as a change of color as viewing angle changes.

For the 1991 model year, it is estimated that nearly 40% of all U.S. automotive OEM coatings contained pearlescent pigments. European and Japanese paint companies are also using pearlescent pigments in their OEM paint formulations.

Pearlescent pigments have been stabilized by various methods to give the durability required for automotive end uses. Panels have been weathered outdoors in Florida and Arizona for five or six years with little or no change in color or gloss. The use of the color base coat and clear top coat now favored in the automotive industry has also added to the gloss and weathering stability of coatings formulated with pearlescent

[2]Brunauer, S., Emmett, P. H., and Teller, E., *Journal of the American Chemical Society*, Vol. 60, 1938, p. 309.

pigments because the clear top coat affords additional protection for the pigmented coat underneath.

Another interesting property that pearlescent pigments optically display is referred to as "geometric metamerism," or "goniochromaticity." These terms mean that the color of the pigments changes as the viewing angle changes. While this is a very desirable attribute from a styling standpoint, it complicates color measurement of coatings that contain pearlescent pigments [*11–14*].

Powder Coatings

Pearlescent pigments have been successfully used in powder coatings for a number of years [*15*]. Since they are nonmetallic in nature, these pigments are free of some of the arcing and flashing problems that occur in electrostatic spray application of powder coatings.

One limiting factor found with the use of pearlescent pigments in powder coatings is their inability to be used in the "melt mix" method of incorporation. This calls for the extrusion of pigments and the powdered polymer to encapsulate the pigment. The use of an extruder is not the problem since pearlescent pigments are extruded in the plastics industry. The problem arises through the use of hammer-mill type mill used to reduce the size of the polymer mass into a powder that will spray through an electrostatic spray gun. Pearlescent pigments must retain their platey or flake-like shape to properly reflect light and produce luster. If these pigments are broken or smashed by milling, the pearlescent effect is greatly reduced. This leaves only dry mixing of the pearlescent pigment and the powdered polymer as an alternative method of incorporation. Such a technique has certain drawbacks such as separation due to different specific gravities, different particle sizes, and so on that can take place due to vibration during shipping, handling, and application.

A new method called the "bonding" method has recently been used with pearlescent pigments and metallic flakes in powder coatings. This technique involves "bonding" of the pigments to the powder by various proprietary methods.

Pearlescent pigments have been used to powder coat automotive wheel covers, bicycles, and outdoor furniture.

Water-Based Coatings

Since pearlescent pigments are chemically very inert and not sensitive to pH, they make ideal pigments for use in water-based coatings. Because of their inert nature, they do not evolve hydrogen gas or react with water-borne systems. Pearlescent pigments are hydrophilic in nature and as such disperse very well in most water-based systems.

Pearlescent pigments have been successfully used in Canada in water-based truck-paint finishes for several years. Currently they are being used as the automotive industry switches from high-solids to water-based coatings with lower volatile organic compound content.

Ink formulations based on water-borne systems have also been developed for both the coated mica and bismuth oxychloride pigments. These are being used in Europe to replace the metallic ink formulation that may be an environmental problem.

Water-based coatings containing exterior grade pearlescent pigments have been tested in outdoor exposure in Florida for three years. These show good weatherability with optimum gloss and color retention.

COLOR MEASUREMENT

Visual

Instrumental color analysis of coatings pigmented with pearlescent pigments is rather difficult. As mentioned earlier, the phenomenon known as goniochromaticity complicates instrumental measurements. As a result, much color observation has been done visually using both draw down cards with nitrocellulose lacquers and coated panels. Comparing a sample and a standard on a black-and-white draw-down card is an effective way of making color comparisons since both the interference color and the absorption color can be seen. Due to the transparency of pearlescent pigments, the color appears different over the black and the white portions of the card.

The interference color can be best seen and visually compared to the standard by looking at the black portion of the draw-down card. The absorption color can be best evaluated and compared by viewing the white portion of the card. Color appears more intense over the black portion because the incident light is reflected and the complementary color is absorbed. On the white portion of the card, the reflected light and the complementary color are both reflected back to the viewer with only a slight diminishing of the specular effect.

Side-by-side draw downs of samples against a standard batch are so effective that they can be used in process control with samples taken at various intermediate stages of the manufacturing process. Also, final quality control judgments can be made using visual assessment of side-by-side draw downs.

Colorimeters and Spectrophotometers

The use of colorimeters and spectrophotometers to measure the color of pearlescent pigmented coatings results in only limited information. Most of these instruments measure at fixed angles of illumination and fixed reflectance angles, such as 0°/45° or 45°/0°. This results in only a portion of the pearlescent color being measured through diffuse reflection. These instruments are not capable of measuring at specular or slight off-specular reflection angles. It is at these near-specular angles that pearlescent pigmented coatings exhibit most of their color through specular reflection.

Colorimeters can be used to measure the bulk color of pearlescent pigments. Highly concentrated draw downs can be made, and the colorimeter readings may be used to determine the bulk color of white and pearl pigments. Colorimeters and spectrophotometers may also be used to measure color on draw-down cards. These data are useful in comparing various batches to each other for quality control and SPC. Color loss from test panels used in accelerated weathering devices and from actual outdoor exposure may be followed using colorimeters and spectrophotometers. Loss of gloss may be followed in weathering test panels with the use of gloss meters at the 20° gloss angle.

Goniospectrophotometers

When the color of coatings with pearlescent pigments or metallic flake is measured, it is necessary to measure at more than one angle. The reason for this is that the color of these types of coatings changes with viewing angle. An instrument capable of making multi-angle color measurements is called a goniospectrophotometer. These instruments are usually capable of changing the angle of incident light (illumination), changing the angle of viewing (reception), or tilting the specimen under investigation. For most of the commercial quality control instruments, only the angle of viewing is changed and the other variables are held constant with the incident-light angle usually fixed at 45°.

Figure 1 shows the viewing angles used in some of these commercial instruments. The optics used are called normalized reflective angles, which means all viewing angles are referred to the specular angle that is sometimes called the gloss angle. Incident light strikes the ample at 45°, and thus the specular angle is also 45°. The near specular angles are usually 15 to 20° off the specular angle to exclude any gloss from affecting the color readings. To completely characterize pearlescent pigmented finishes, it is necessary to measure at least three angles. This is usually near specular, i.e., about 15 to 20° off specular, at 45° off specular, and at several far diffuse angles, usually 70 to 115° off specular. All commercially available goniospectrophotometers will measure reflected light at a minimum of three angles, and several instruments measure at more angles, with one measuring at twelve angles. Research goniospectrophotometers that allow angle variation of about 5° off specular to 110° in five-degree intervals are also commercially available.

The importance of measuring at more than one angle is apparent from Figs. 2 and 3. In Fig. 2 the reflection curves taken at near specular angle are nearly identical, whereas in Fig. 3, when this same set of panels was measured at a diffuse angle, markedly different reflection curves are obtained. These data were obtained using one gold interference pearlescent pigment to which a small amount of phthalocyanine blue had been added and another gold interference pearlescent pigment to which a small amount of phthalocyanine green had been added. At the near specular angle, the gold interference color is apparent, and, since both coatings used the same gold pigment, the two curves are nearly identical. However, at the diffuse angle, the colors of the organic pigment added to the pearl finish are now apparent, with one curve typical of a blue and one curve typical of a green colorant. If this same pair of panels were presented to a conventional 0°/45° colorimeter, the readings would be of a blue and a green colorant with no information obtained about the color due to the gold pearlescent pigment.

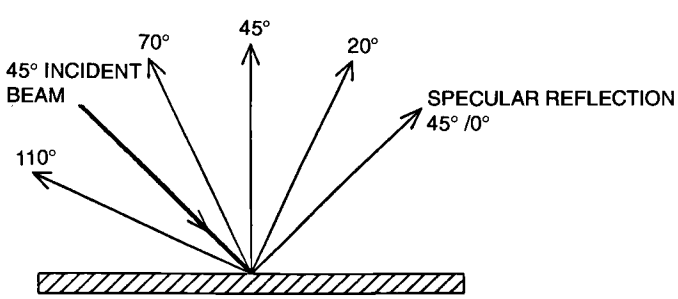

FIG. 1—Normalized reflection angle schematic for a commercial goniospectrophotometer.

Figures 4, 5, and 6 are reflection data for the color of panels coated with solid color, metallic flake, and pearlescent pigment, respectively, as a function of viewing angle. These curves were obtained at 14 viewing angles from 10 to 110° off specular with a research-type goniospectrophotometer. From Fig. 4, it is apparent that the solid color, i.e., nonmetallic or pearlescent, does not change appreciably with viewing angle, so conventional colorimeters and spectrophotometers measuring at 0°/45° can be used to obtain information about coating color. Figure 5, which contains reflection data for the metallic-flake (aluminum) pigmented coating, has a change in the lightness (L) value with angle, but has very little change in the chroma values (a and b). Adding organic colorants to metallic flake will increase the chroma change. The reflection data in Fig. 6 demonstrates the change in color as a function of viewing angle of a blue interference color pearlescent pigment. Changes in the chroma values are readily evident. In Figs. 4, 5, and 6, L^*, a^*, and b^* are the CIE 1976, International Commission on Illumination 1976, apparent-color scales, ASTM Standard Terminology on Appearance (E 284).

ASTM has a task group under E-12.03.02 developing a specification for visually and instrumentally measuring the color of metallic and pearlescent pigments. In addition to development of an instrumental method for measuring the color of such pigments, the task group is also involved in having a visual method approved. Recently one of the instrument companies has developed a color-matching booth especially designed for color matching these types of pigments. This booth contains a combination of three differently positioned light sources, and rotation of the sample panels through five different angles will provide 15 viewing geometries ranges from 10 to 110° off specular. This visual color matching booth should provide color matchers with a new tool for studying metallic and pearlescent pigmented finishes.

TESTING

Weatherability Testing

Weatherability tests with pearlescent pigments take the form of both accelerated and outdoor testing. Accelerated testing includes use of such devices as QUV exposure chambers, condensation testers, and water-bath soaking. Outdoor testing may include exposure in Florida and/or Arizona at 5° South or Black Box. Specimens consist of painted metal test panels, pieces of pearlized plastic film, or injection-molded, pigmented parts.

Color and gloss readings are made on the original test panels before exposure, and panels are exposed in replicates. Panels are removed from the test fences at various times and tested for changes in color and gloss. Testing with the stabilized exterior grades of pearlescent pigments usually goes on for at least five years, and the panels are viewed and examined every six to twelve months. Such testing has shown that exterior-grade pearlescent pigments have the capability of standing up to the weathering stresses found in modern automotive coatings along with other exterior uses. Accelerated

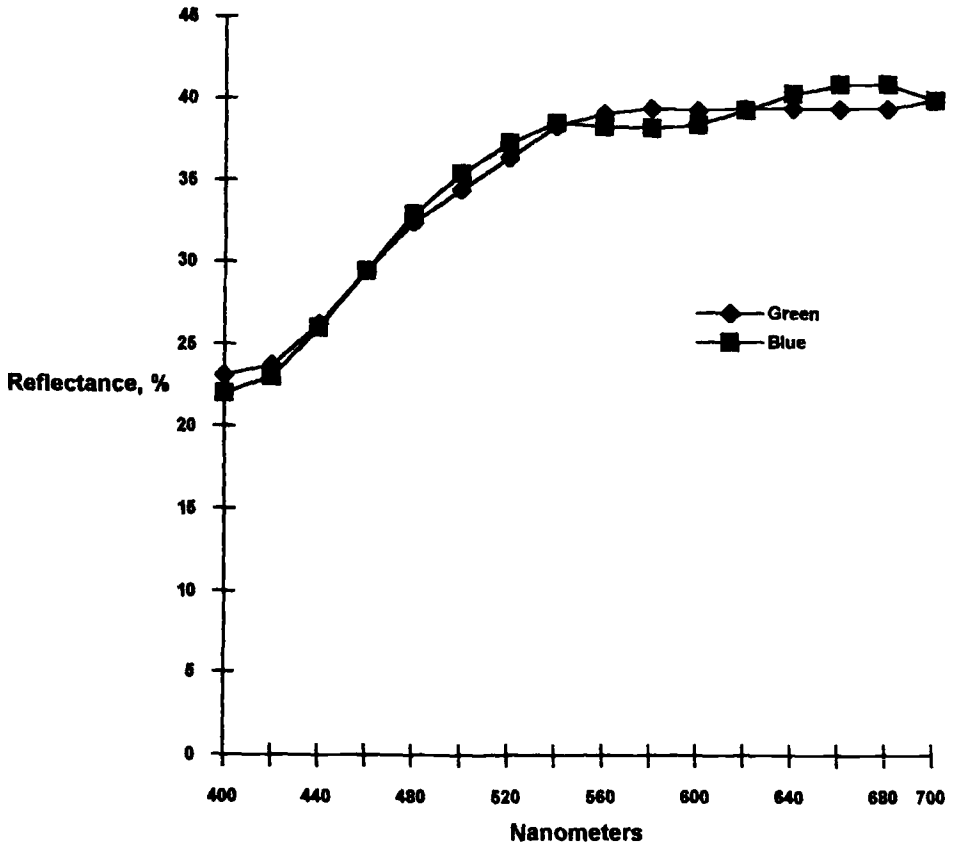

FIG. 2–Reflection as a function of wavelength at near the specular angle for a gold pearlescent pigment containing a blue or a green colorant.

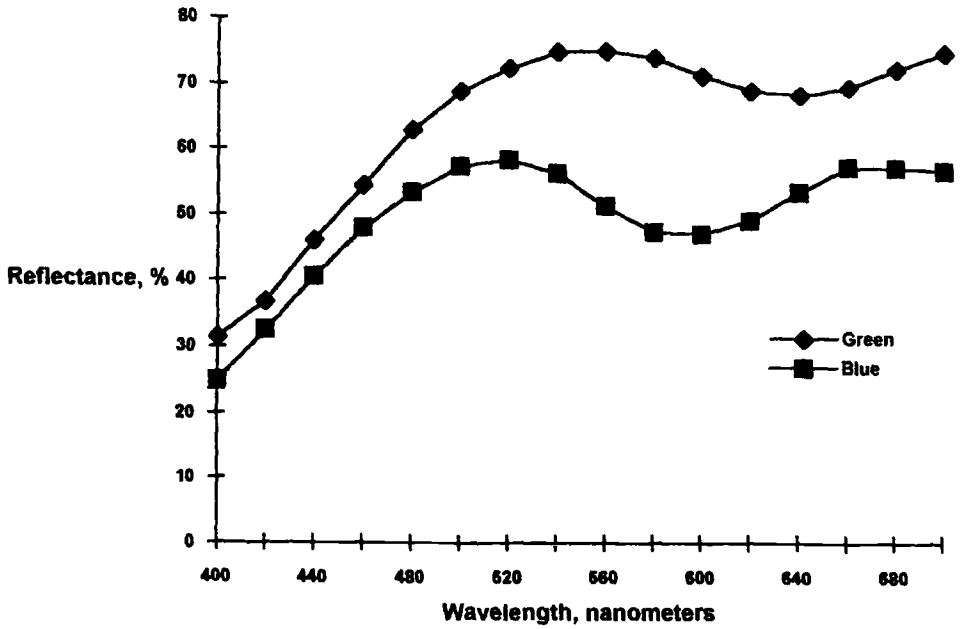

FIG. 3–Reflection as a function of wavelength at a diffuse angle for a gold pearlescent pigment containing a blue or a green colorant.

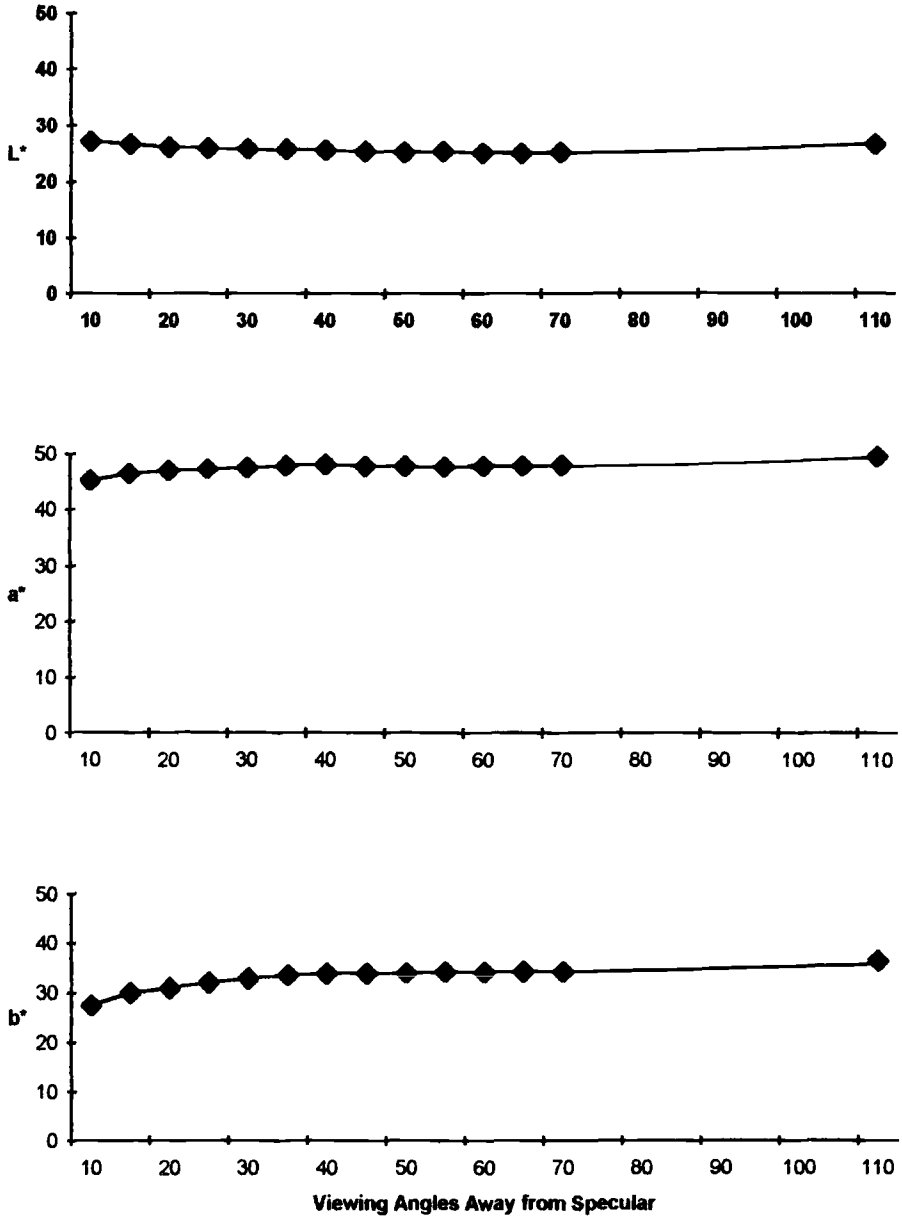

FIG. 4—Variation of color in a solid color-coated panel as a function of viewing angle.

weathering has proven to be reliable and capable of differentiating between the stabilized exterior grades and the untreated types generally used in plastics or inks.

Particle Size

Early methods for determining the particle-size distribution of pearlescent pigments involved manually counting particles viewed under a microscope. The microscopist usually counted about 1000 particles, grouped them in 5-μm intervals, and then created a distribution curve. The technique was tedious and time consuming, plus it did not give enough statistical data about the large particles.

More modern methods that have been tried include the Coulter Counter, automated sedimenters, and sieving. Most had difficulties because of the shape of pearlescent pigments, i.e., they are flakes with very thin thickness and very broad surfaces. These pigments are roughly the same size as metallic flake pigments, but they are much larger in size than organic colorants and most inorganic pigments. The most successful instruments found thus far for measuring particle size of these pigments are the laser diffraction types. These give good relative measurements. The numbers obtained, however, are not absolute values since the theory for these devices is based on spherical particles and not platelets. Calibration of these laser diffraction instruments with standardized glass spheres have shown them to be reliable and reproducible with pearlescent pigments.

As mentioned above, pearlescent pigments are classified into particle-size distributions for various end uses. Automotive coating sizes are carefully controlled by sieving to remove any particles over 50 μm. Such large particles can lead to

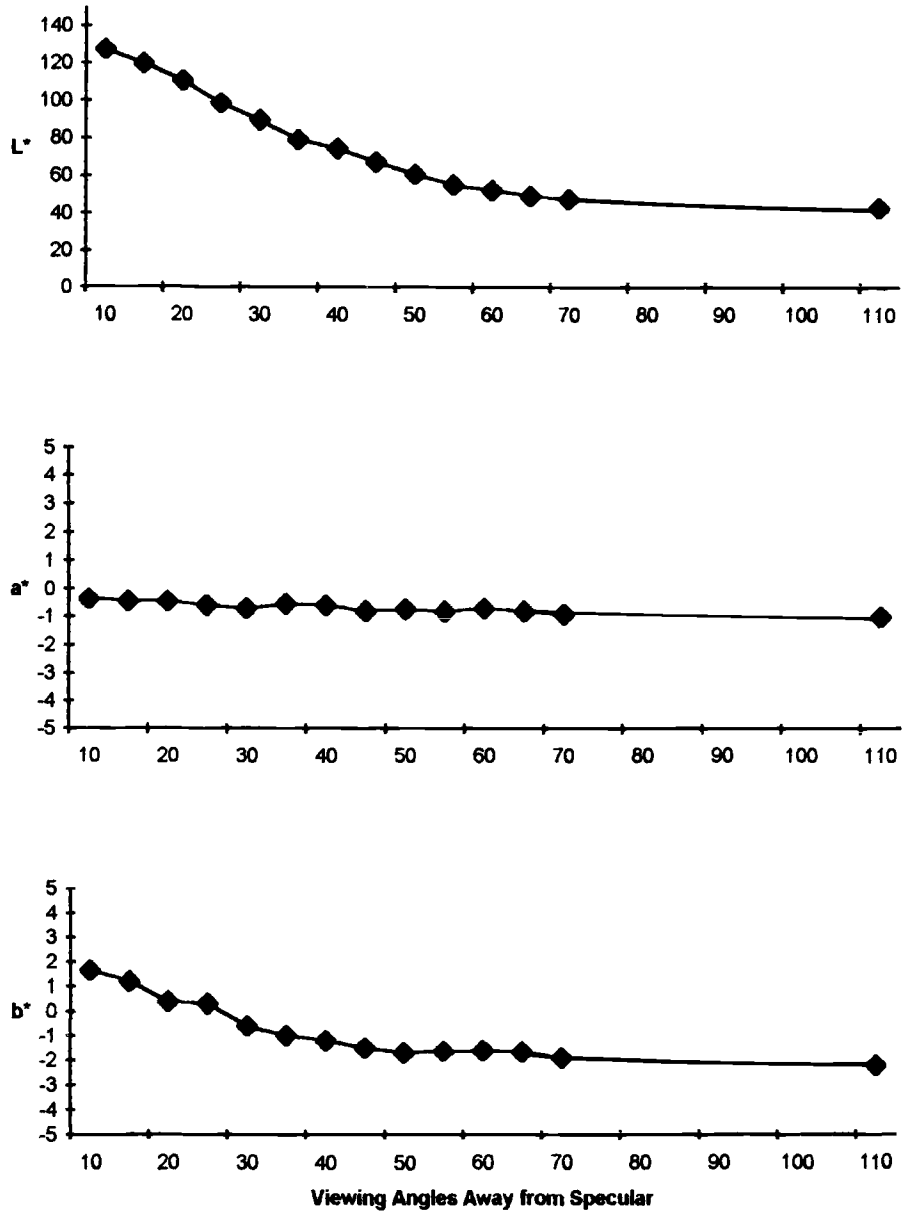

FIG. 5–Variation of color in a metallic flake-coated panel as a function of viewing angle.

clogging of filters in automotive painting operations. Very fine particle sizes are required for some applications such as offset ink formulations and some low solids, water-based coating systems. Particle sizes of pearlescent pigments range from about 5 to 20 μm for fine grades and up to 100 to 150 μm for the coarse grades.

Chemical Testing

Chemical testing of pearlescent pigments consists of analyses of the chemical composition, i.e., percentage of TiO_2 or ferric oxide (Fe_2O_3), of mica, and of other ingredients. Also, trace analyses for heavy metals such as lead, arsenic, Cr^{+6}, are done by atomic absorption, ICP instrumentation, and X-ray fluorescence. Both extractions in 0.5 *N* HCl and total dissolution methods are used in these analyses. Extraction methods usually give less than 20 ppm lead and 3 ppm arsenic in pearlescent pigments. Other tests performed include conductivity, pH in aqueous solution, specific gravity, bulk density, and, when a solvent is present, flash point.

HEALTH AND ENVIRONMENTAL CONSIDERATIONS

Pearlescent pigments are nontoxic and nonmetallic materials that do not exhibit the arcing and conductivity usually associated with metals. Lead and arsenic contents are less than 20 and 3 ppm, respectively. All ingredients are Toxic Substances Control Act (TSCA) listed. The health hazard rating for dry pearlescent pigments are:

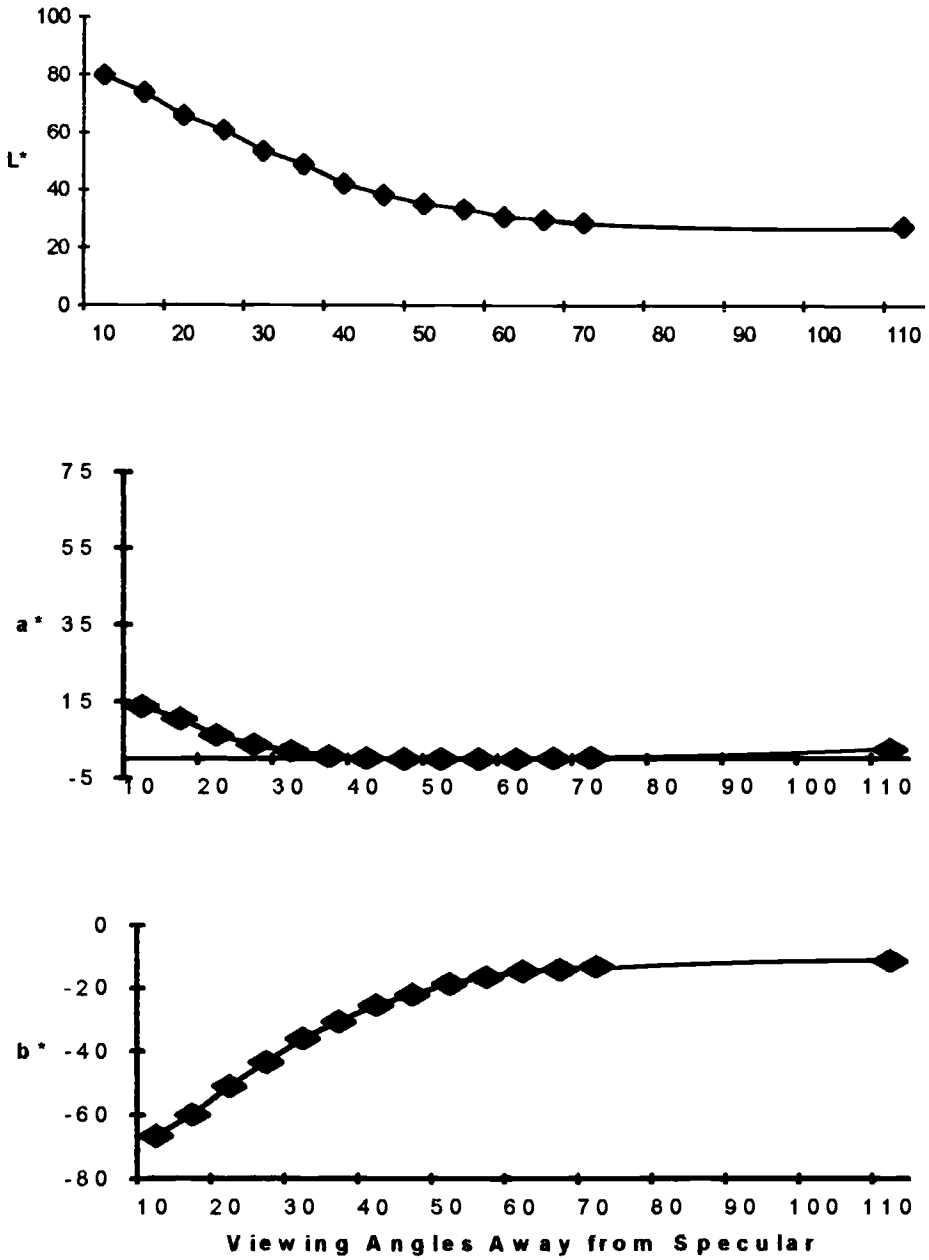

FIG. 6–Variation of color in a pearlescent pigment-coated panel as a function of viewing angle.

Health—O
Flammability—O
Reactivity—O
Personal Protection—E

If dusting occurs when handling the dry products, a dust mask should be worn. Several grades are also available in a "wetted out" form to produce nondusting products. Many pearlescent pigments have been used for years in cosmetic applications. These cosmetic grade pearlescent pigments have FDA approval for use as cosmetic ingredients and color additives.

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Inorganic Anti-Corrosive Pigments

by M. Jay Austin[1]

WHAT IS CORROSION?

CORROSION IS AN ELECTROCHEMICAL PROCESS that takes place on the surface of metals, deteriorating them and—if not halted—destroying them. The process usually occurs in a liquid or gaseous environment and may take the form of a direct chemical attack, electrochemical reaction, electrolysis, or oxidation. During deterioration, the metal may form compounds or be taken into solution. The following factors must be present for corrosion to take place:

- A thermodynamically unstable metal.
- An electrolytic conductor of ions.
- An electrolyte (an electrical conductor such as a moist path).
- An electron acceptor.

If corrosion is extreme, the metal will, in essence, return to the more stable composition of its original ore, disintegrating into oxides, carbonates, and sulfates. For instance, the rusting of iron metal occurs naturally under atmospheric conditions, since rust, a hydrated form of the common iron ore, ferric oxide, is more stable than iron metal [*1*]. In this example, the unstable iron metal is also an electrical conductor. Salt water is usually the electrolytic conductor of ions, and dissolved oxygen is the electron acceptor [*2*].

Rates of corrosion vary, often depending on the electrolyte. Normally, metallic surfaces in contact with acidic solutions (such as salt water [*3*]) will exhibit the most rapid rate of corrosion; neutral solutions will be somewhat less corrosive and alkaline solutions the least corrosive. Metal may also corrode in the presence of soil or a dissimilar metal [*4*]. While many types of corrosion exist, this discussion is limited to the degradation which occurs when a metal's natural protective oxidative film is attacked and worn away.

Common examples of this sort of corrosion include the progressive red rusting of iron, the white rusting of zinc, and the tarnishing of copper.

THE USE OF COATINGS TO PROTECT METALS AGAINST CORROSION

Before the beginning of recorded time and ever afterward, mankind has battled corrosion with a multitude of methods and mechanisms. For our purposes, we will limit our discussion to examination of the following five mechanisms of protecting metals by using coatings:

- Barrier effect of film or vehicle.
- Barrier pigment effect.
- Sacrificial pigments.
- Vehicle enhancement (film formulation and development).
- Active inorganic inhibitive pigmentation.

Barrier Effect

Among the oldest inhibitive methods known, barrier coatings provide a protective, physical shield between a metal and air, moisture, or chemicals. While the composition and thickness of barrier coatings vary widely, they generally have a low permeability or moisture vapor transmission rate. As a rule, the lower the transmission rate, the less likelihood that oxygen and moisture will reach the substrate. Some common barrier coatings include organic paints and lacquers, metallic coatings (hot dip), and heavy mastics.

Barrier Pigment Effect

Pigments not only add color to coatings but can also protect metal from corrosion by reinforcing the film and limiting permeability. "Lamellar" pigments, for example, such as mica and micaceous iron oxide, form a wall of flat, thin particles within a paint film. These resist penetration, forcing water to wend a long, tortuous path toward the substrate (Fig. 1). Metallic flakes of aluminum, bronze, or steel produce similar effects.

Since not all pigments are compatible with all resin systems, care must be taken when adding pigments to a coating. In highly acid or alkaline environments, inert or chemically resistant pigments should be used.

Sacrificial Pigments

Zinc is a "natural" for use in protective coatings since zinc-rich coatings offer cathodic protection when applied to ferrous substrates, that is, the zinc acts as a cathode during the corrosion process, receiving the attack normally suffered by the ferrous metal [*5*]. To some degree, the duration of the pigment's efficacy is dependent on the thickness of the sacrificial coating.

Vehicle Enhancement

The formulation of a coating itself can add greatly to corrosion protection. The addition of pigments, for example, can

[1]Vice President and technical director, HALOX Pigments, a division of Hammond Lead Products, 1326 Summer Street, Hammond, IN 46320-2240.

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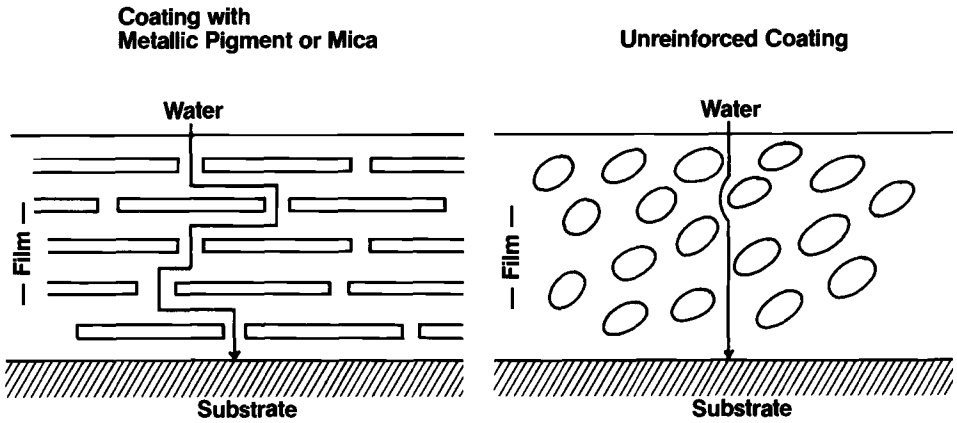


FIG. 1–Barrier pigment effect. Water takes a straight path through an unreinforced film, but is forced to take an extended path through lamellar particles of a metallic flake or mica-reinforced film (after Alan Smith, *Inorganic Primer Pigments* [*2*]).

help reinforce film structure and reduce permeability (as mentioned earlier). Some pigments, such as red lead, react with components in linseed oil/alkyd primers to produce lead soaps which increase the corrosion resistance of the paint film [*6*]. Other additives are used to enhance other coating or film characteristics, such as drying time, flow, adhesion, and mildew resistance. Binder selection and manufacturing methods may also be adjusted to offer maximum corrosion prevention.

Inorganic Inhibitive Pigments

The majority of this chapter will focus on the following active inorganic inhibitors: borates, chromates, leads, molybdates, phosphates, phosphites, and silicates. These pigments help prevent corrosion by increasing the likelihood of a chemical reaction which can produce a protective coating on the surface of a metal or otherwise foiling the chemical reaction between metal and corrosive solution. The ability to render a metal surface passive is called *passivation* and is covered here in two forms: (1) cathodic/anodic and (2) oxidative.

Cathodic and Anodic Passivation—Inhibitive inorganic pigments minimize corrosion in neutral solutions by acting as polarizing agents to retard the three elements of the corrosion process: cathodic reactions, anodic reactions, and ionic currents in the solution and the metal itself [*7*].

Since the cathodic and anodic processes are the basis for the corrosion process, control of these processes can play an important role in corrosion inhibition. The cathodic process consists of electrons passing from the metal to an electron acceptor, such as oxygen or hydrogen ions at the negative terminal, or cathode. In the anodic process, metal ions pass into the solution at the positive terminal, or anode (Fig. 2).

As polarizing agents, inhibitive pigments work in a variety of ways. Some slow the electrolytic process by retarding the reactions through *resistance polarization*, that is, by increasing a film's electrical resistance on the surface of the anode or cathode [*8*]. Some inhibitors, such as zinc, magnesium, and manganese, form insoluble deposits with hydroxyl ions in neutral solutions at the cathode. These deposits create a visible film on metal surfaces and help increase cathodic resistance polarization. Some inhibitors work in acid solutions, enhancing polarization by raising the concentration of positively charged hydrogen ions at the cathode.

Inhibitive pigments such as zinc chromate, phosphate, silicate, and borate suppress corrosion by enhancing anodic passivation in acid solutions. In neutral solution, the pigments are adsorbed onto the metal surface, reducing anodic activity.

Oxidative passivation—Though oxidation is usually thought to contribute to the deterioration of a metal, oxidation sometimes creates a protective layer on a metallic surface. Passivation can occur if a metal is oxidized to a stable compound that is part of the electrolyte [*9*]. Consider, for example, the protective layer of aluminum oxide on aluminum metal. The oxide minimizes atmospheric corrosion despite the reactive nature of the metal.

Strong oxidizing conditions are normally required for passivation to occur. Take the case of iron and nitric acid. Exposed to concentrated nitric acid, iron will develop a very thin inhibitive passive film; dilute nitric acid, however, will attack the metal [*10*].

Neutralization—Another mechanism of inhibitive pigments is neutralization of corrosive substances as sulfates, acids, and chlorides. This can often be achieved through the use inhibitors in a basic environment, which decrease the corrosive effect of acids and enhance the precipitation of corrosive elements.

SOME WELL-KNOWN INORGANIC ANTI-CORROSIVE PIGMENTS

Coatings industry suppliers are developing high-performance inorganic pigments to meet the growing demand for nontoxic inhibitive coatings that are both economical and highly effective. The section that follows discusses the chemistries, physical properties, functions, advantages, and disadvantages of some of the most common inorganic inhibitive pigments.

Wherever available, the specific gravity, color, pH, oil absorption, and water solubility of each pigment is recorded, supplied in most cases from pigment manufacturers' published data. Large discrepancies can exist between such data

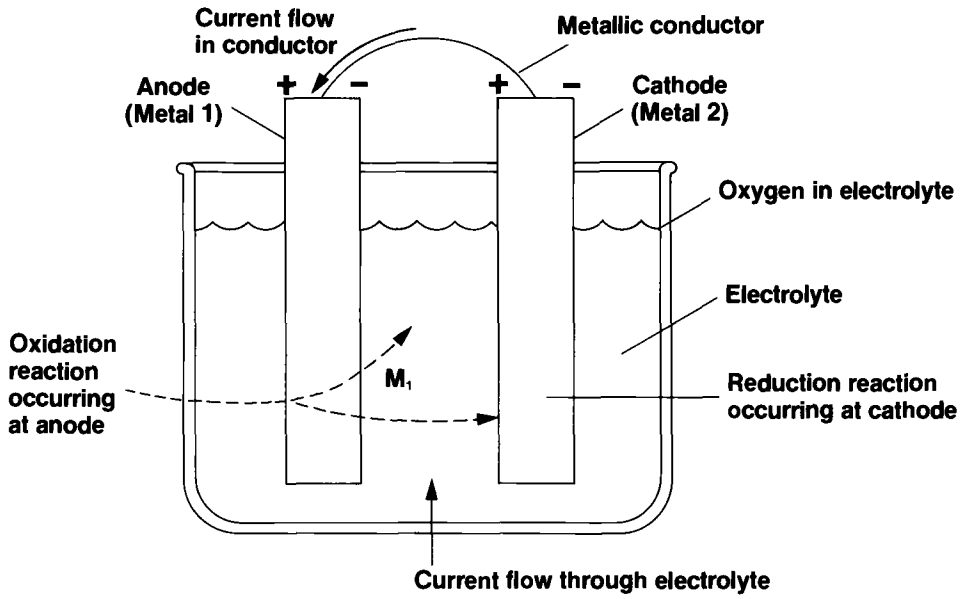


FIG. 2–Electrochemical corrosion. A simple cell showing the components required for cathodic and anodic corrosion processes (after Dean Burger, "Fundamentals and Prevention of Metallic Corrosion," *Corrosion and Corrosion Protection Handbook,* Philip A. Schweitzer, Ed., Marcel Dekker, Inc., New York and Basel, 1983).

and actual measurements, and verification of the published data is therefore recommended before any formulation project is initiated since significant differences in data can dramatically affect formulation performance. This author, for example, measured oil absorptions as high as 85 for some zinc chromate samples, although the published data report an oil absorption of approximately 25.

For the following pigments, *specific gravity* is expressed as g/cm^3; *color* indicates general appearance; *pH* is measured on a 10% slurry; *oil absorption* is expressed as g/100 g and normally determined by the spatula rubout method, ASTM D 281-84; and *water solubility* is expressed as percent soluble. Recommended loading levels for many of the pigments are also included for general formulation assistance, and these are expressed as a percentage of total weight based on typical paint density of 1200 g/L or 10 lb/U.S. gallon. If paint densities vary widely from these figures, simple extrapolations may be made.

Borates

A. Barium Metaborate ($BaO{\cdot}B_2O_3{\cdot}H_2O$) [*11-14*]

The grades shown in Table 1 indicate three grades of commercially available modified barium metaborate, the most commonly used borate inhibitor. Grade I is the primarily barium metaborate, and Grades II and III are modifications of Grade I which are said to decrease the reactivity of the pigment, thus increasing its formulation versatility. Grade II includes approximately 27% zinc oxide, and Grade III includes approximately 18% zinc oxide and 29% calcium sulfate.

Modified barium metaborates may be used in many kinds of applications in a broad range of solvent and water-based resin systems. The pigment's alkalinity contributes to inhibition, and the anodic passivation from the metaborate ion adds to the pigment's anti-corrosion performance.

TABLE 1—Typical properties of modified barium metaborates.

	Grade I	Grade II	Grade III
Specific gravity	3.30	3.70	3.30
Color	White	White	White
pH	10.0	9.1	10.0
Oil absorption	30	20	23
Water solubility	0.3%	0.2%	0.4%
Typical loading levels:	3 to 15%, based on total weight. Some heavy duty maintenance coatings may require up to 40%		

Barium metaborates are often considered environmentally acceptable alternatives to more traditional, toxic pigments; however, it must be remembered that soluble barium is an acute toxicant, and its presence in high levels may cause pigments to be classified as hazardous wastes.

The pigment has other disadvantages. As a soluble compound, it may be quite reactive with many systems. To control its solubility, it is often coated with a silica modification. When barium metaborate is formulated with certain acidic resins or acid-catalyzed baking systems, the resultant coating may exhibit stability problems. Therefore, care must be taken when formulating water-reducible and latex resin systems using this pigment to minimize its solubility and reactivity.

B. Zinc Borate

Zinc borate, usually used to provide flame retardancy in plastics and cellulosic fibers, is not normally thought of as an inhibitive pigment. However, recent research indicates that zinc borate, used in combination with modified barium metaborate or zinc phosphate, exhibits synergistic performance properties resulting in enhanced corrosion prevention. This

effect is most likely the result of the blended product's decreased solubility.

Chromates

Chromates have long been used as inhibitors since the soluble chromate ion is itself inhibitive and the chromate passivating ion is among the most efficient passivators known. Unfortunately, chromates are less widely used than in the past since hexavalent chromium pigments are either confirmed or suspected human carcinogens [*15*]. Evidence indicates that strontium, calcium, and zinc chromates are among the most carcinogenic forms of hexavalent chromium. Also, lead chromate is considered a suspected carcinogen by the American Conference of Governmental Industrial Hygienists (ACGIH), while zinc chromate is considered a confirmed carcinogen [*16*].

A. Zinc Potassium Chromate ($4ZnO{\cdot}6K_2O{\cdot}4CrO_3{\cdot}3H_2O$)

Specific gravity	3.45
Color	Yellow
pH	7.5
Oil absorption	25
Water solubility	0.1% [*17*]

This inhibitive pigment, also known as zinc chromate or zinc yellow, is the product of reactions among potassium dichromate, zinc oxide, and sulfuric acid. Versatile and highly efficient, zinc chromates are effective inhibitors even at relatively low loading levels. Because of their yellow color, they are generally limited to use as primers.

Although zinc chromates have a threshold limit value of 0.001 mg/m^3 and are therefore fairly toxic, these pigments are among the most widely used anti-corrosive products. In the United States, they still make up more than 30% of the entire inhibitive pigment market.

How do zinc chromates prevent corrosion? While the specific mechanism is not wholly understood, there are several theories on the subject, i.e.:

- Zinc chromates are anodic inhibitors.
- Zinc chromates improve the corrosion protection of the existing oxide film [*18*].
- The ferrous salts precipitated by zinc chromates contain a protective mixture of ferric and chromic oxides.

B. Zinc Tetraoxychromate ($ZnCrO_4{\cdot}4Zn[OH]_2$)

Specific gravity	3.65
Color	Yellow
pH	7.5
Oil absorption	53
Water solubility	<0.01%

Often referred to as basic zinc chromate, zinc tetraoxychromate is commonly used in the manufacture of two-package poly(vinyl butyryl) (PVB) wash primers, which consist of phosphoric acid and zinc tetraoxychromate dispersed in an alcoholic poly(vinyl butyryl) solution. These primers, also called etch primers or tie coats, are used to passivate steel, galvanized, and aluminum surfaces, improving the adhesion of topcoats. Because they are usually low in solids and are applied at fairly low film thicknesses, these wash primers have very poor hiding ability.

C. Strontium Chromate ($SrCrO_4$)

Specific gravity	3.70
Color	Yellow
pH	8.5
Oil absorption	35
Water solubility	0.05%

Strontium chromate is mainly used to prevent corrosion on aluminum, and primers containing this pigment are standard for the aviation industry. Strontium chromate is so effective at low loadings that it is often used to provide inhibition for coil coatings despite the fact that it is the most expensive chromate inhibitor.

The pigment is sometimes combined with zinc chromate in water-based formulations. In these cases, to avoid stability problems, loadings are kept at low levels, about 2% total chromate.

D. Other Chromate Inhibitors

Barium chromate, calcium chromate, and ammonium dichromate are also used to control corrosion and flash rust, but their use is very limited and merits no further discussion here.

Leads

Lead, though not a direct inhibitor, reacts with certain resin systems to form lead soaps which *are* active inhibitors. Lead pigments have proven themselves over the years to be outstanding anti-corrosives which perform particularly well over insufficiently prepared surfaces.

However, since it accumulates in body tissue, lead is generally considered an acute and chronic toxicant and has become the subject of strict environmental regulations, especially regarding waste disposal and worker protection. Although they are still used to produce heavy duty maintenance coatings and lead chromate colors, regulations have caused the use of lead pigments to decline.

A. Red Lead (Pb_3O_4)

Specific gravity	8.85
Color	Orange
pH	6.5
Oil absorption	6
Water solubility	<0.001%

One of the first recorded inhibitors and still one of the most effective, red lead has been widely used in primers for structural steel. The pigment is available in four grades containing from 85 to 98% Pb_3O_4.

While red lead is an oxidizing agent, its inhibitive mechanism is much more complicated than mere oxidation. When formulated with linseed oil, red lead forms soaps which, in the presence of water, release soluble lead compounds and organic acids. These soaps also improve the mechanical properties of the paint film and promote passivation through three mechanisms:

- Anodic adsorption of soluble lead compounds.
- Anodic adsorption of acid molecules.
- Anodic precipitation by oxidation [*19*].

Although soap formation is red lead's chief protective mechanism, use of the pigment is not restricted to oil-based paints. Epoxides, chlorinated rubbers, and vinyls are just some of the "oil-less" systems which are often formulated using red lead. There are questions regarding whether red lead functions as an inhibitor in these systems. It is more likely that the pigment exhibits the low oil absorption, pigment packing characteristics, and fine particle size of an ideal extender.

B. Basic Lead Silicochromate (BLSC)

Specific gravity	4.1
Color	Orange
pH	—
Oil absorption	14
Water solubility	<0.01%

Developed as a substitute for red lead, BLSC was once widely used in heavy duty maintenance coatings. It contains two active ingredients: monobasic lead chromate and gamma tribasic lead silicate. The former enhances the stability of the coating package and contributes a chromate ion, thus improving inhibition; the latter provides exceptional inhibitive characteristics.

BLSC offers several advantages over red lead:

- Reduced density minimizes problems with pigment suspension and settling and lowers the density of finished paint.
- Improved resistance to chalk and carbonation for better weather resistance and application in topcoats.
- Lower tint strength for a broader range of color formulation.

Because it contains both lead and hexavalent chromium, BLSC is no longer as widely used as it once was.

C. Other Lead Pigments

The following lead-based products have been used to inhibit corrosion in very specific or very limited applications: lead suboxide; basic carbonate white lead and lead cyanamide (mirror back coatings); basic lead silicate (electrodeposition primers); tribasic lead phosphosilicate; basic lead silicosulfate; dibasic lead phosphite; lead chromosilicate; lead sulfate; and calcium plumbate.

Molybdates

Molybdate-based pigments are anodic passivators, preventing corrosion by forming a protective layer of ferric molybdate on the surface. This layer is insoluble in neutral and basic solutions. However, since most commercial molybdate pigments contain zinc, the formation of inhibitive zinc soaps in oleoresinous systems may add to the anti-corrosive properties of molybdate products.

Although molybdate inhibitors are free of lead and chromate, they are limited in market value due to their expense. To make these more accessible, molybdate/phosphate compositions have been introduced, though these are difficult to disperse. Micronized versions of molybdate/phosphate are available to counteract the dispersion problem.

Following are the four most popular molybdate inhibitors available on the market today.

A. Basic Zinc Molybdate [20]

Specific gravity	5.06
Color	White
pH	6.5
Oil absorption	14
Water solubility	<0.01%
Typical loading levels	5 to 15%

Recommended for use in alkyds, epoxides, epoxy esters, polyesters, and other solvent-based resin systems.

B. Basic calcium zinc molybdate [21]

Specific gravity	3.0
Color	White
pH	8.5
Oil absorption	18
Typical loading levels	2.5 to 10%

Recommended for use in water-reducible and latex-based resin systems as well as two-component polyurethane and epoxy systems.

C. Basic Zinc Molybdate/Phosphate [22]

Specific gravity	4.0
Color	White
pH	5.5
Oil absorption	14
Water solubility	<0.01%

Recommendations are the same as for basic zinc molybdate. This product, however, is reported to provide enhanced performance over rusted steel substrates.

D. Basic Calcium Zinc Molybdate/Zinc Phosphate [23]

Specific gravity	3.0
Color	White
pH	7.5
Oil absorption	18
Typical loading levels	5 to 15%

This inhibitor, a mixture of basic calcium zinc molybdate and zinc phosphate, is reported to offer improved adhesion over ferrous metals. Recommended for use in both solvent- and water-based systems.

Phosphates

A. Zinc Phosphate [$Zn_3(PO_4)_2 \cdot 2H_2O$]

Specific gravity	3.2
Color	White
pH	7.5
Oil absorption	25
Water solubility	<0.01%
Typical loading levels	5 to 10% in water-based systems; 5 to 15% in solvent-based industrial systems; 10 to 30% in maintenance coatings

Zinc phosphate's formulation versatility has probably led to its status as one of the most widely used "nontoxic" inorganic inhibitors. Zinc phosphate can be readily used in a wide

variety of resin systems, including high acid number alkyds, water-reducible coatings, high-performance resins and acid-catalyzed baking systems. The pigment's low reactivity and low solubility give it a distinct formulating advantage over more basic, less stable nontoxic pigments.

Zinc phosphate is thought to inhibit corrosion in three ways:

- Through phosphate ion donation.
- By forming a protective anodic film.
- By forming anti-corrosive extracts in the presence of certain oleoresinous vehicles.

Zinc phosphate has a creditable track record of effective performance in real-world testing, but rates much lower in salt spray testing and other accelerated tests. This poor performance may be explained by the fact that salt water and high humidity often impair the performance of the pigment.

B. Modified Zinc Phosphates [24,25]

The coating industry has produced several variations of zinc phosphate that make use of other inorganic inhibitors and organic surface treatments to improve the pigment's performance in salt spray testing. The formulation versatility and recommended loading levels of these modified versions of zinc phosphate are about the same as those of standard unmodified zinc phosphate. Although the modified zinc phosphates appear to offer improved performance in accelerated testing, there is little evidence to uphold these claims in actual commercial applications.

Modified versions of zinc phosphate include:

Aluminum zinc phosphate—The higher phosphate content and solubility of this aluminum/zinc coprecipitated phosphate contribute to its enhanced corrosion inhibition.

Basic zinc phosphate hydrate—An organic surface treatment (claimed to be an electrochemically effective inhibitor) enhances the performance of this pigment.

Basic zinc molybdenum phosphate—This pigment makes use of a low level of molybdate (1.5%) to enhance inhibition.

Zinc silicophosphate hydrate—This pigment appears to be a complex composite of barium sulfate, silica, magnesium oxide, and sodium dichromate. Trace amounts of hexavalent chromium may account for the pigment's improved performance, but even these very low chromate levels could possibly present waste disposal problems.

C. Aluminum Triphosphate [26]

Available commercially in three grades (Table 2), aluminum triphosphate is a relatively recent chromate-free inhibitor. A condensation product, it is often modified with zinc ion or silicate to minimize its solubility and reactivity. Inhibition is thought to result from the tripolyphosphate ion's ability to chelate iron ions, as well as higher phosphate levels resulting from the depolymerization of the tripolyphosphate ion into orthophosphate ions. These pigments exhibit typical phosphate performance relative to loading levels.

Each grade is recommended for specific applications:

Grade I—For use in solvent-based primers (alkyds and epoxides). Grade I is modified with zinc and silicate.

Grade II—For use in solvent and water-based systems. The pigment's lower water solubility apparently makes it more suitable for water-based coatings. Grade II is modified with zinc and silicate.

Grade III—For solvent and water-based systems. Easier dispersion makes the pigment more effective in low build coatings. Grade III is modified with zinc.

TABLE 2—Typical properties of aluminum triphosphate.

	Grade I	Grade II	Grade III
Specific gravity	3.0	3.1	3.0
Color	White	White	White
pH	6.5	6.5	6.5
Oil absorption	37	32	30
Water solubility (max)	1%	1%	1%

Phosphites

A. Zinc Hydroxy Phosphite $\{[2ZnO(OH)_2 \cdot ZnHP_3O_3] \cdot X_2H_2 \cdot O$, where X = 1 to 17$\}$ [27]

Specific gravity	3.9
Color	White
pH	7.0
Oil absorption	18
Water solubility (Max.)	0.04%
Typical loading levels	10-25% in maintenance applications; 5-15% in general industrial and water-based applications

Zinc hydroxy phosphite (also called zinc phospho-oxide) results from the reaction between zinc oxide and phosphorous acid. Anodic passivation of the phosphite ion is the primary mechanism of inhibition, although the pigment's ability to form inhibitive zinc soaps in oleoresinous systems also contributes to corrosion prevention. While not recommended for use in high-acid-number or water-soluble resins, the pigment is compatible with a variety of resin systems.

Silicates

Silicate pigments contribute to corrosion inhibition in several ways, chiefly through anodic and cathodic passivation. In addition, in oleoresinous systems, these pigments form inhibitive soaps of barium, calcium, strontium, and zinc. The inhibitive value of silicate pigments is further enhanced by their alkalinity and solubility.

A. Calcium Borosilicate [28-30]

Available in three commercial grades (Table 3), calcium borosilicate is effective in a range of applications:

a. *Grades I and III*—Recommended for use in protective coating systems-based on traditional alkyd technology, these pigments differ primarily in their B_2O_3 content: 10.6% for Grade I and 15.6% for Grade III. They are generally used for such applications as trade sales, industrial maintenance, railroad and tank coatings, and shop primers. While they can be used in a variety of resin systems, including medium and long oil alkyds, epoxy-esters, and modified alkyds, they are not suited for use in high-acid-number resins, acid-catalyzed systems, water-based

TABLE 3—Typical properties of calcium borosilicates.

	Grade I	Grade II	Grade III
Specific gravity	2.65	2.71	2.65
Color	White	White	White
pH	10.1	10.1	10.1
Oil absorption	36	27	41
Water solubility (max)	0.35%	0.34%	0.37%
Typical loading levels	10–20%	10–20% in primers, 2.5–10% in topcoats and DTM finishes	10–20%

resins, epoxides, and other high-performance resins, or for immersion or semi-immersion service.

b. *Grade II*—This pigment, a low-oil-absorption version of the other two grades, is used primarily in high solids, medium gloss topcoats, direct-to-metal (DTM) coatings, and self-priming alkyd systems. PVC levels range from 40 to 45% in primers and 15 to 25% in topcoats and DTM coatings.

B. Phosphosilicates [31-34]

Four modifications (see Table 4), each representing a different commercial grade, are available for a variety of uses.

Calcium Barium Phosphosilicate (Grade I)—This pigment is for use in conventional and high solids solvent-based epoxy systems. The pigment is also used in organic zinc-rich primers as an anti-settling agent.

Calcium Barium Phosphosilicate (Grade II)—A low-oil-absorption version of this pigment, Grade II is for use in most water-borne systems, including latexes and water-reducible systems. When formulated in alkyds, this product, like many other phosphate pigments, will demonstrate excellent real-world performance, but poor performance in accelerated testing.

Calcium Strontium Phosphosilicate (Grade III)—This pigment is for use in most water-based acrylic lacquers, as well as water-reducible caulks and sealants. When the product used with zinc phosphate in water-based lacquer systems in a 1:1 ratio, a synergistic effect is produced which improves performance.

Calcium Strontium Zinc Phosphosilicate (Grade IV)—This grade is for use in a broad range of resin systems, including traditional and high-solid alkyds, latexes, epoxides, water-reducible alkyds, high-acid-number resins, vinylidene chloride latexes, and catalyzed baking systems. A recent development, Grade IV is the most versatile and effective of the phosphosilicate inhibitive pigments. Because of its fine particle size and low oil absorption, this pigment is effective in thin film applications and in systems requiring a high gloss.

TABLE 4—Typical properties of phosphosilicate inhibitors.

	Grade I	Grade II	Grade III	Grade IV
Specific gravity	2.97	2.97	2.90	3.01
Color	White	White	White	White
pH	7.9	8.3	7.8	7.0
Oil absorption	44.5	31.5	53.5	26.0
Water solubility	0.02%	0.02%	0.03%	0.02%
Typical loading levels	5–10%	5–10%	5–10%	2.5–15%

Miscellaneous Inhibitive Pigments

A. Ion Exchange Pigment

Specific gravity	1.8
Color	White
pH	9.2
Oil absorption	50 [35]

Claimed to be effective in all paint systems, this pigment uses the mechanism of ion exchange with corrosive species to prevent corrosion. Loading levels should be half the levels of typical corrosion-inhibiting pigments.

B. Zinc Oxide

Research has suggested that zinc oxide possesses both passivating and cathodic inhibitive capabilities [36,37]. Also, when used in latex metal primers and certain oleoresinous systems (such as SSPC Paint No. 25) [38], zinc oxide exhibits obvious anti-corrosive action.

Often used with more conventional active inhibitors such as zinc chromate and calcium borosilicates, zinc oxide appears to raise the cross-link density of many paint films, making them harder. Zinc oxide may also absorb ultraviolet light, thus protecting the resin. Since the pigment tends to have seeding problems and can cause film brittleness, care must be taken when using zinc oxide in inhibitive coating applications.

Zinc Metal in Primers

The prime focus of this discussion is inorganic inhibitive pigments which function through the mechanism of soluble inhibitive species; however, zinc metal—which functions through the mechanism of cathodic protection—deserves a brief mention.

In many applications, including the protection of steel structures, zinc-rich coatings offer the best corrosion inhibition available, especially when topcoated with either epoxy or urethane. Actual particles or flakes of zinc in the paint film protect the ferrous substrate by acting as the anode and corroding sacrificially. While the correct loading level of zinc metal in zinc-rich primers is still a matter of debate, these coatings usually contain 80 to 85% zinc metal. Zinc-rich primers can be formulated as inorganic coating systems (ethyl silicate binders) or organic systems (such as epoxides).

Zinc-rich primers require near-white blast surface preparation and must be fully cured before topcoating. Two major problems associated with zinc-rich formulation are pigment settling and hydrogen gassing.

Barrier Pigments

A. Aluminum Flake

Aluminum flake, typically supplied as a slurry, is produced by atomizing molten aluminum and ball-milling the powder into a solvent. The resultant flake is frequently used to improve the appearance and anti-corrosion performance of

coatings for tanks, bridges, roofs, railroad cars, automobiles, and office equipment.

Coatings containing aluminum flake stand up well to heat and moisture. They also resist the damaging effects of ultraviolet light, cooling the substrate and preventing deterioration of the binder.

Aluminum flake is available in two grades, leafing and nonleafing. A stearate coating on the leafing grade allows the pigment to float on the surface of a paint film. Because this coating is also associated with intercoat adhesion failure in primer coats, leafing grade aluminum flake is normally used in topcoat formulations. Typical loadings range from 20 to 25%. A disadvantage of using aluminum flake is that the pigment is very reactive with water, and hydrogen gassing may occur if moisture levels are not maintained below 0.15%.

B. Steel Flake

Stainless steel and a number of steel alloys are sometimes used to make steel flake, which is used in coatings for applications requiring maximum resistance to abrasion.

C. Micaceous Iron Oxide (MIO)

Specific gravity	4.9
Color	Dark Gray
Oil absorption	11
Typical loadings	30-50%

A naturally occurring form of hematite with an Fe_2O_3 content of about 92 to 95%, MIO has been used in protective coating formulations for over 100 years. Because of its lamellar structure, it is typically used in primers to improve their barrier resistance. Used in topcoats, MIO enhances resistance to ultraviolet light.

ENVIRONMENTAL CONSIDERATIONS

Health and safety factors have always been seriously considered during the development and evaluation of new protective coatings. Use of lead, hexavalent chromium compounds, and other toxic pigments is constantly monitored to ensure that current, acceptable limits are met. Environmental regulations have driven the inhibitive coatings industry to increase efforts to develop and evaluate new, nontoxic products to replace lead, chromates, and traditional inhibitors with long-standing performance records.

Two primary environmental concerns within the industry are worker protection and waste disposal. Several steps have been taken to ensure worker safety. For example, all workers have the right to know the dangers involved with handling the materials they are exposed to every day and the right to be offered the capability to handle these materials safely. Because absorption of toxic pigments through inhalation is a major concern, workers are protected by engineering controls (ventilation), respiratory controls (masks, filters, and other equipment), and extensive safety training. The preferred option is to completely eliminate the hazardous material and substitute a less toxic pigment, if possible.

Waste disposal pertains to plant waste produced by paint manufacturing and waste from painting operations. The latter includes overspray and spent blast abrasives contaminated with lead and chromate-based pigments. Under these regulations, containment and disposal of these materials could well increase the cost of a typical maintenance repainting project by tenfold. Regulations concerning the disposal of industrial wastes in the United States are strict, due in part to revisions of the Drinking Water Regulations of the Safe Drinking Water Act, which is an effort to prevent contamination of the water supply.

The coatings industry is under legislative pressure to develop environmentally acceptable, high-performance, long-lasting replacements for lead and chromate-based pigments and reduce levels of VOC. These are not easy tasks. Some of the formulation and application factors which affect the industry's efforts at compliance have already been discussed; the following is a look at some of the stringent techniques in use to evaluate the performance of new, less toxic inhibitors and protective coatings.

HOW FORMULATION AFFECTS THE PERFORMANCE OF INHIBITIVE PIGMENTS

When formulating with inhibitors, a host of formulation factors must be taken account since these factors often determine the selection of inhibitive pigments and greatly affect the development of inhibitive coatings. The most critical formulation factors include PVC (pigment volume concentration), selecting an extender pigment, solubility and reactivity (that is, selecting a vehicle and understanding how its components interact), and the complex interrelationships between all these factors.

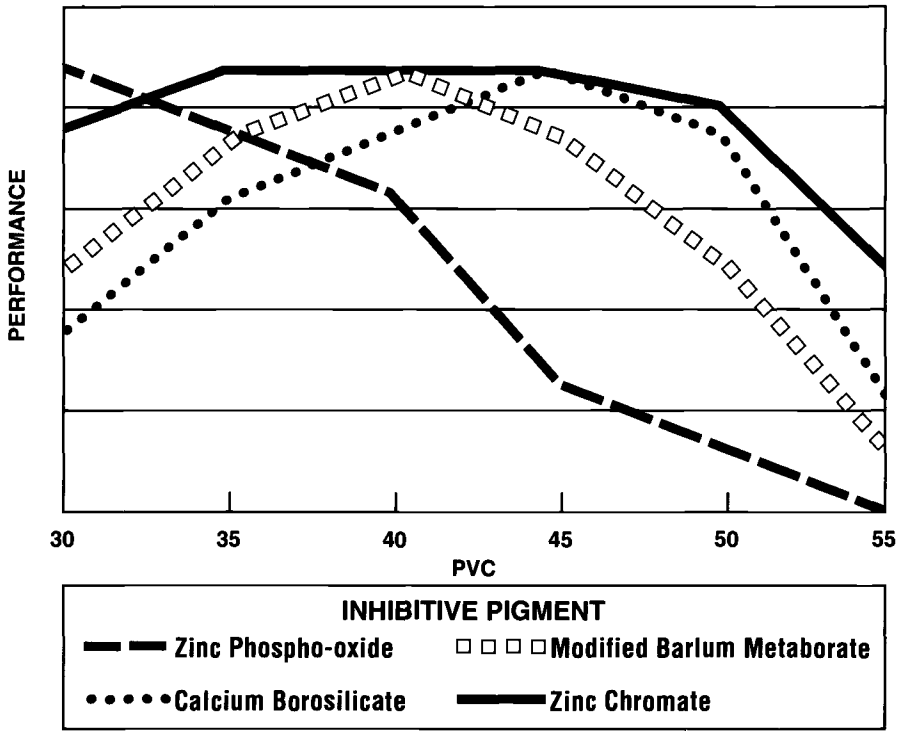
Pigment Volume Concentration

Pigment volume concentration (PVC) is the ratio of pigment volume to the total nonvolatile volume in a coating. Probably the most important formulation factor to consider when evaluating anti-corrosive pigments, PVC is especially crucial when two or more inhibitors are being considered for a given application.

Essential to the understanding of the importance of PVC is the concept of a "formulation window." This term represents the PVC range at which an inhibitive pigment will give its best performance and is clearly depicted in Fig. 3. Here, the performance in a salt fog cabinet of three popular chromate-free inhibitors is compared to that of zinc chromate in a medium oil alkyd primer. Loadings are equal—about 10% of total formula weight—across a PVC ladder at constant volume solids.

In the figure, the three nontoxic inhibitors each yielded performance equivalent to zinc chromate, but only within a specific PVC range, a rather narrow formulation window. Conversely, zinc chromate offered far greater formulation versatility, performing over a much broader PVC range.

The figure illustrates both the importance of addressing the variable of PVC and poses a problem facing the formulator: None of the environmentally acceptable inhibitors—including the three in the figure—come close to matching the traditional lead and chromate-based pigments for overall efficiency and formulation flexibility. While each of the three chromate-free inhibitors was formulated to equal the per-



PVC Loading Levels (Formulation Windows) of Chromate-free Inhibitors and Zinc Chromate

FIG. 3—Medium oil alkyd PVC ladder: salt spray performance. Formulation windows of four inhibitive pigments.

formance of zinc chromate, each performed at a much narrower formulation window, thereby severely restricting its use.

Many factors influence the formulation window of an inhibitive pigment in a given formulation. All these factors must be satisfied to maximize the performance of an inhibitor. Crucial factors to consider in association with PVC are: (1) specific gravity, oil absorption, and other physical properties of an inhibitor; and (2) the effect of these properties on CPVC (critical pigment volume concentration).

The concept of CPVC, introduced in the late forties, postulates the existence of a level of pigmentation in a dry paint film at which there is just enough binder to coat the pigment particles and fill the spaces between them [*39,40*]. Since many nontoxic inhibitors are lower in specific gravity and higher in oil absorption than more traditional inhibitors, it is easy to formulate anti-corrosive coatings which exceed CPVC and therefore deliver unacceptable levels of inhibition. To avoid this situation, it is necessary to evaluate inhibitive pigments across a PVC range to achieve optimum performance. To do this, coatings should be made at each extreme of the PVC range; then weight blends of these paints may be used to generate the intermediate levels.

Inhibitor Loading Levels

In the "old days" of inhibitive coatings formulations, before the advent of environmental regulations, the rule of thumb was to add as much inhibitive pigment as possible. The assumption: if a little was good, then a lot must be better. This "rule" worked as long as formulators used red lead and other lead-based pigments whose very high specific gravities and low oil absorptions permitted relatively high loadings. When large amounts of nonlead inhibitors are used in formulations, the resulting coatings often perform well in accelerated corrosion tests. However, most nonlead inhibitors are much more reactive in vehicle systems than lead-based inhibitive products, and this reactivity can lower the actual performance of coatings formulated with high inhibitor loadings.

In general, inhibitor loading should be carefully balanced, keeping in mind that more is not necessarily better, at least as far as less-toxic, more-reactive inhibitors are concerned.

Comparing inhibitive pigments—Certainly not as straightforward a matter as comparing apples to oranges, comparing pigments may be accomplished in several different ways: on the basis of equal volume, equal weight, equal cost, or equal performance. The choice of method can drastically affect the results of a formulator's evaluations.

Equal Volume—This is the easiest evaluation method and by far the least desirable. Replacing a given volume of one inhibitor with the same volume of another is simple and requires the least number of formulation changes. However, the wide variations in specific gravities of inhibitors (from a low of 2.5 to a high of 9.1) and oil absorptions, which vary from 10 to 70, make the results of these evaluations highly questionable.

Equal Weight—This is a valid method of evaluating inhibitors with loading levels equal to or exceeding 120 g per liter

(1 lb/gal). Care must be taken to adjust the levels of extender pigment and vehicle solids when replacing one inhibitor with another. This is to ensure that the inhibitors can be compared at a constant loading level over a given PVC range at constant volume solids.

Equal Cost—This method is valid if the inhibitor levels are less than 120 g per liter (1 lb/gal), as long as comparisons are conducted at a constant loading level over a PVC range at constant volume solids.

Equal Performance—The most tedious approach, this method ensures the most cost-effective formulation possible. Basically a combination of simultaneous evaluations of a PVC ladder and an inhibitor loading ladder, this approach permits the formulator to evaluate each inhibitor for its optimum formulation window.

Extender Pigments

Although a wide choice of extenders is available for inhibitive coatings formulation, extender selection traditionally has not received much attention. This may be the result of the former widespread use of lead and chromate-based inhibitors, whose excellent performance masked any flaw contributed by an extender. With emphasis on environmentally acceptable (and less effective) inhibitors, however, selection of suitable extenders is an important factor in the formulation of inhibitive coatings.

Figure 4 contains the results of work in latex maintenance coatings. The data here clearly show that the performance of extender pigments depends to a great extent on the type of vehicle and inhibitor used in the formulation, that is, the performance of extenders will vary from system to system. Selecting the appropriate extender, therefore, may be as crucial to coating performance as selecting the vehicle system or inhibitive pigment [*41*].

Reactivity and Solubility

Inhibitors should be carefully selected for compatibility with given coating systems to prevent common formulation problems arising from reactivity and solubility. For example, a pigment must have some solubility within a given system in order to participate actively in passivation. Also, a highly reactive pigment can react with binders and other ingredients in a coating system, causing instability. Adverse chemical reactions between the inhibitor and the vehicle in the can or the cured paint film can effect coating properties such as viscosity, drying time, cure, adhesion, and weatherability. Therefore, inhibitive pigments must be chosen carefully to prevent these formulation problems [*42*].

Some chemical reactions, such as the reactions between basic pigments and acid catalysts, neutralize inhibitive action by preventing film cure. Some reactions may even accelerate corrosion. Others may do good or harm, depending on *where* they occur. For example, the formation of metallic soaps on a paint film caused by a reaction between red lead and linseed oil acids promotes corrosion inhibition; however, if this same reaction occurs in the paint can, viscosity may increase to the point that the liquid paint becomes unusable.

Generally, inhibitive pigments retard or prevent blistering caused by corrosion in pinholes or scribes or by moisture drawn into the paint film by electrical activity of the corrosion cells. But use of inhibitors may lead to osmotic blistering, especially during humidity and condensation testing. Osmotic blistering is caused by the presence of water and soluble pigment at the juncture of the substrate and the coating film [*43*]. To prevent this condition, low-solubility pigments should be used.

APPLICATION AND PROTECTIVE COATING PERFORMANCE

Coating application (how, where, why, and for how long a coating will be used) must be carefully considered when formulating environmentally acceptable alternatives to traditional toxic inhibitors. The length of time a protective coating can effectively protect a ferrous surface has been said to

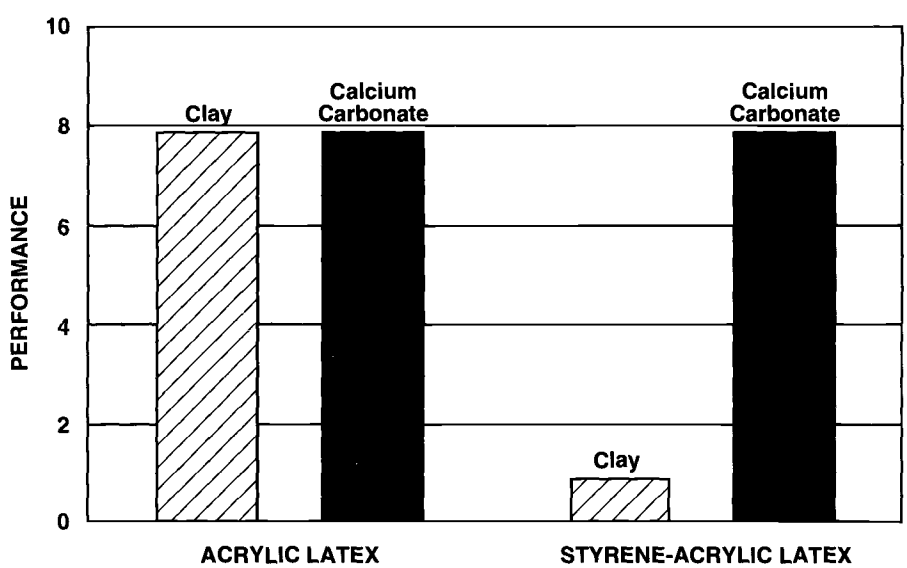


FIG. 4–Extender performance properties: accelerated performance measurements.

depend on the following application factors: the environment, how the coating is applied, the substrate, and the surface preparation of the substrate [*44*].

Consider the environment where the inhibitive coating will be used: Will the coating be exposed to harsh chemicals, abrasion, industrial atmospheres, heavy traffic, high heat, or other extreme conditions? Or will it be used in a rural setting, exposed to the elements? Answering these questions will help determine the proper vehicle system and application techniques to be used with the coating.

Other factors to consider when deciding how to apply a protecting coating include the type of applicator (brush, roller, spray, or dip), adequate and uniform film thickness [*45*], drying time, and temperature. Though application techniques are often given little attention, they can profoundly affect the performance of a protective coating.

Substrates are also important factors in testing protective coatings and inhibitive pigments. For example, untreated cold rolled steel generally shows more undercutting at scribes than sandblasted hot-rolled steel or treated steel. Because it is easier to differentiate between pigments on untreated steel, that substrate is frequently used to compare the performance of different inhibitive pigments. On the other hand, use of a phosphatized substrate seems to improve the performance of protective coatings, apparently enhancing adhesion, passivating the surface, and improving the coating's inhibitive properties.

A word of caution: When selecting substrates for testing inhibitive coatings systems, care must be taken to conduct final evaluations of a system on the substrate that the coating will be applied to in actual use. For screening purposes, however, evaluations may be conducted on any appropriate substrate.

Protective coatings are frequently applied to the following ferrous substrates [*46*]: cold-rolled steel; polished cold-rolled steel; zinc phosphate-treated cold-rolled steel; iron phosphate-treated cold-rolled steel; hot-rolled steel; abrasive blasted hot-rolled steel; pre-rusted hot rolled steel, and galvanized steel.

No matter what the substrate, the surface preparation of the substrate, or its condition, is vital to the evaluation of protective coatings and an important factor in determining the life expectancy of a coating system. In addition to cleaning a surface, improving adhesion, and maximizing the performance of the inhibitive pigment, surface preparation helps remove contaminants—such as chlorides and sulfates—from the substrate's surface [*47*].

Though many methods of surface preparation exist, their effectiveness varies widely. For example, studies suggest that a protective coating will last four times longer on a blasted surface than on a hand-cleaned or weathered substrate [*48*]. This improved longevity is attributed to better adhesion and a more intimate contact between substrate and coating, which allows the inhibitor to maximize its performance.

Some of the commonly used surface cleaning techniques are [*49*]: centrifugal blasting; metallic and nonmetallic abrasives; abrasive air blasting and water blasting; by hand and power tools; chemicals; pickling. Less common methods include hot gas, flame, bacterial, zinc shot, ice particles, and ultrasonic.

EVALUATING INHIBITIVE PIGMENT AND COATING PERFORMANCE

Pigment and coating evaluation techniques—especially accelerated laboratory tests—are more important now than ever before. The reason: Users and manufacturers alike demand that new inhibitive products not only meet environmental regulations, but also meet or exceed the performance standards set by established, environmentally unacceptable pigments. This discussion will deal with the two principle methods of evaluation used by the coatings industry: accelerated testing and "real-world" (natural atmospheric) testing.

Accelerated Corrosion Testing

In real-world applications, protective coatings are often expected to provide up to 20 years of service. Accelerated testing attempts to predict the life expectancy of a protective coating in a short span of time, from half a year to a year. This evaluative "fast forwarding" meets the needs of manufacturers and users alike, who demand prompt development and commercialization of new products. Though several kinds of accelerated testing procedures are in use, all have essentially the same purposes: to significantly shorten the time needed for a coating to fail and to evaluate the causes of its failure.

Although accelerated corrosion testing is the most commonly used evaluation method for inhibitive pigments and protective coatings, the results of accelerated tests correlate poorly with the results of real-world testing. Because of this, the validity of accelerated testing, particularly the salt spray test, has been the target of serious doubts and questions. Is accelerated testing relevant to real-world conditions? Do the tests accurately predict product performance? Evidence is growing to support the theory that many formulation variations used to enhance a coating's salt spray performance may actually detract from the coating's real-world performance.

It has already been demonstrated that, in many cases, accelerated testing is an unreliable predictor of a coating's long-term protective performance. Figure 5 clearly illustrates this deficiency, depicting salt spray results which totally contradict the results of natural exposure testing for two protective coatings.

Despite such strong evidence against the reliability of the salt spray test, its popularity continues. For good or bad reasons, it is the driving force behind the establishment of performance evaluation criteria for many protective coating systems and is often the *only* criterion used to evaluate an inhibitive coating. In some cases, raw material suppliers are forced to offer products based solely on their salt spray performance, often without regard to the coatings' performance in the real world. Another section of this book discusses this situation further and details the research the industry is doing to address the problem.

Real-World Corrosion Testing (Natural Atmospheric Exposure Testing

Considered by many researchers to be the most dependable method of predicting the performance of a protective coating, real-world testing exposes products to real-time, actual atmospheric conditions. In essence, the tests approximate the types of environments for which the coatings were designed.

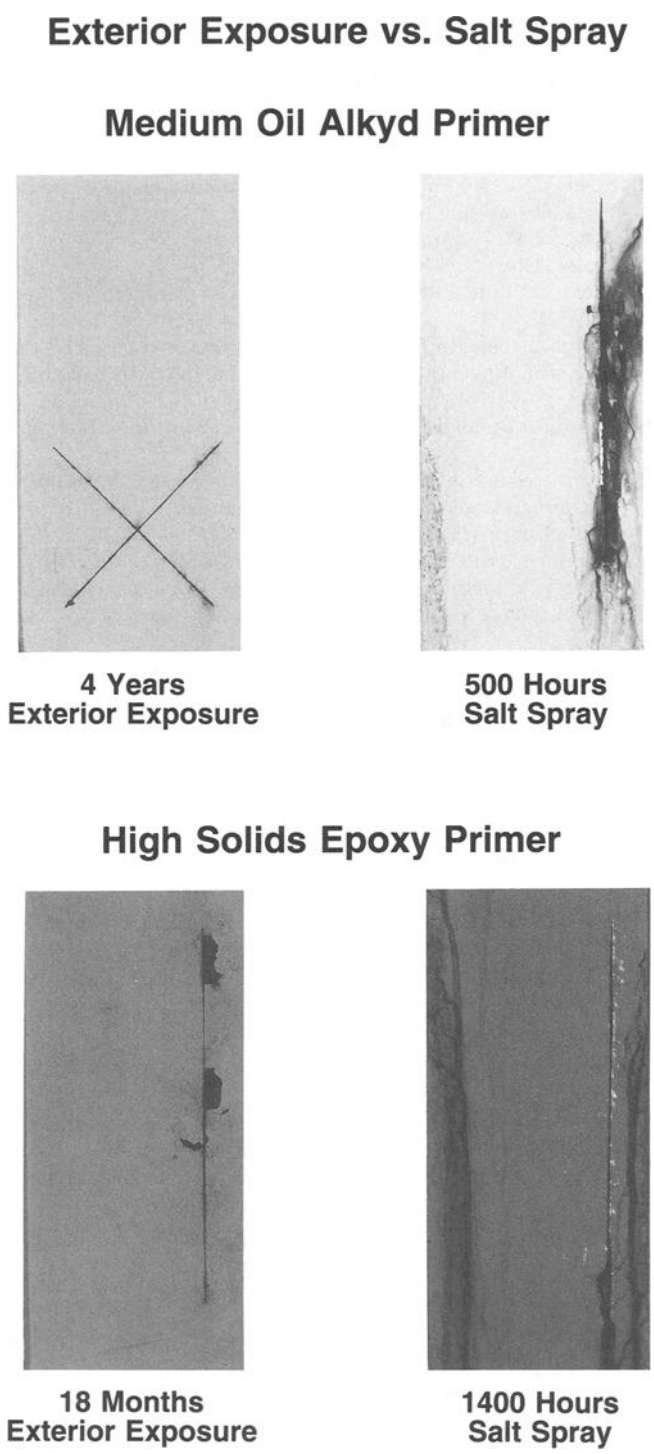


FIG. 5—Protective coating performance data.

Despite their excellent ability to measure and predict anti-corrosive coating performance, outdoor exposure tests have four obvious disadvantages compared to accelerated tests [*50*]:

1. *Long Duration*—Monitoring the degradation of protective coatings is a marathon task lasting from 5 to 20 years. To accelerate the rate of failure in outdoor exposures, testing labs have exposed the paints to very harsh environments or applied the coatings at lower-than-recommended film thicknesses. Neither of these procedures are effective, however, since neither represents the application for which the coating was designed.
2. *Lack of Controls*—Establishing controls and measuring a coating's consistency of performance is a real challenge in real-world testing. In outdoor exposures, environmental factors such as temperature and humidity change from year to year at the same site, making reproducible results next to impossible.
3. *Multiple Stresses*—Because a coating exposed to an outdoor environment encounters many stresses, it is not easy to determine the effects of each individual stress.
4. *Varying Environments*—In outdoor testing, establishing a standard test environment is virtually impossible. Environments vary dramatically from one part of the country to the other, from desert to seashore, from mountains to alluvial plains. Local industries and fluctuations in weather patterns also contribute to the problem.

In spite of these drawbacks, real-world testing is emerging as a viable alternative to traditional accelerated testing. Even comparatively brief exposures of six to eight months can yield important data. However, the value of these data depends on sound experiments and proper evaluation techniques. Formulators can no longer depend on "one paint/one panel" test designs.

Statistical Analysis

Another method of correlating performance data and predicting coating performance is the use of statistical analysis, which is growing in popularity. Various techniques used to design more meaningful, accurate evaluations include correlation methods, survival analysis, curve fitting, time series analysis, and reliability and life analysis.

Several techniques have been developed for assessing macroscopic damage to protective coatings. Though coatings have traditionally been assessed by visual inspection, these procedures can apparently detect early stages of corrosion, giving more relevant, accurate information in a shorter exposure period.

RECENT TRENDS AND DEVELOPMENTS

New Product Development

The Federation of Societies for Coatings Technology (FSCT) monitors the development and performance evaluations of many new products, many of which reflect the trend toward less toxic inhibitors [*51*]. Another growing trend is the development of products with lower oil absorption, necessary for the formulation of high solids vehicles.

Because proper use of auxiliary extenders can enhance inhibitive properties of protective coatings (especially those incorporating nontoxic inhibitors), the trend toward developing auxiliary extender pigments is likely to continue. Auxiliary pigments are standard extenders modified by surface treatments of silanes, titanates, ziconates, and other compounds. Some commonly used auxiliary pigments include calcium carbonates, clays, talcs, silicas, and wollastonite.

Other Testing Procedures

Driven by changing regulatory standards and the industry's need for prompt product development, a variety of alternative accelerated testing procedures are being researched and developed. The challenge is to make accelerated testing accurately reflect real-world conditions and yield meaningful, realistic results. The Corrosion Committee of the Federation of Societies for Coating Technology (FSCT) commissioned a survey [*52*] on this subject directed to manufacturers and users of protective coatings. The results of the survey showed that the participants were exploring the use of the following kinds of modified accelerated testing techniques: (1) cyclic tests; (2) cyclic natural exposures; (3) electrochemical testing; and (4) physico-chemical, physical, and mechanical testing procedures.

The Steel Structures Painting Council (SSPC) is evaluating the most promising of these accelerated cyclic corrosion tests. The survey itself is too extensive to be included here but is readily available from the FSCT.

CONCLUSION

Before the beginning of recorded history and ever since, protecting ferrous surfaces from the disintegrating effects of corrosion has been one of mankind's most common and perplexing battles. From the lead compound Homer's blacksmiths smeared on their wagon wheels to the sophisticated protective coatings used today, the science of preventing corrosion is as complex as the corrosion process itself. Over the years, many factors have arisen which demand consideration: substrate selection, surface preparation, vehicle and pigment selection, and PVC, to name just a few.

Now the coatings industry is engaged in a new approach to the age-old corrosion-protection problem: developing effective new nontoxic inhibitors to take the place of traditional lead and chromate-based pigments. The research is well underway, and the next ten years may well see the widespread acceptance of these safe, high-performance alternatives. This progress will be accomplished not by scientific curiosity or commercial demand alone, but also by concern for the protection of our fragile human habitat.

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28

Oil Absorption of Pigments*

by Joseph V. Koleske[1]

MIXING A PIGMENT WITH LINSEED OIL and making a paste is a preliminary test applied to pigments that has been in use in a systematic manner for almost a century and perhaps even longer in a less defined manner. Results from the test are usually qualitative in character and give an approximation of color and texture. If the test is conducted in a quantitative manner, the amount of oil needed to make a stiff paste is obtained. It has been felt that the oil absorption test is a measure of an oil-based paint's resistance to flow or consistency. For example, Mills [*2*] indicated that if equal volumes of "oil absorption paste" are mixed or thinned with equal volumes of thinners, the paints prepared have equal resistance to flow, viscosity, or consistency. Also, Stieg [*3*] found that if the oil absorption value is determined by the ASTM rub-out method (described below) and expressed on a volume basis, it is proportional to the critical pigment volume concentration. This test is also related to the pigment packing factor (PPF) and critical pigment volume concentration (CPVC).

MECHANISM

When the oil absorption test is performed, the surface of each pigment particle is wet and saturated to a certain extent with oil and thus is encased in an oil shell that has been estimated to be as thick as eight molecules [*3,4*]. The amount of oil needed depends on the specific pigment area, which is a function of particle size, roughness, and porosity. With temperature and humidity constant, the oil adsorption value depends on the duration and vigor of the rubbing operation and on the affinity of the oil for the pigment. As oil is added beyond the particle encasement stage, the interstices between the oil-encased particles become filled with oil. The amount of oil required for this stage of the test is a function of the type packing taken on by the particles. Packing can range from rhombehedral to cubic. In addition, the presence of aggregates, which are clusters of pigment not broken up by the rubbing process, and agglomerates, which are clusters of pigment formed after the pigment has been wet, have an effect on the amount of oil needed. Agglomeration is affected by the nature of the oil, and linseed oil that meets ASTM D 234: Specification for Raw Linseed Oil [*5*], except that it should have an acid number of 3 ± 1, is used. More extended discussions of oil absorption theory and practice can be found in the literature [*6–10*].

METHODS FOR DETERMINING OIL ABSORPTION

There are two ASTM methods for determining oil absorption that will be described briefly as well as related methods that, for the most part, are tabulated and referenced (Table 1).

Gardner-Coleman Method

This classical method or some variation of it [*11*] has been in use for about three quarters of a century. The current method, ASTM D 1483: Test Method for Oil Absorption of Pigments by Gardner-Coleman Method [*12*], has been in use for over 32 years. In this test, a soft paste is formed from the pigment by drop-wise addition of raw linseed oil with an acid number of 3 ± 1 from a burette to the gently stirred pigment. As the oil is slowly added, the mixture is continuously stirred and folded so the oil strikes dry pigment as long as any remains. The mixture is not vigorously rubbed as in the rub-out method. Eventually the mixture collects in small lumps that gradually coalesce. The rate of oil addition is reduced as the end point is reached. The amount of oil required to form a paste is used to calculate the oil absorption value. The end point for paste formation is taken to be the point when the lumps of wet pigment form a single ball or when an excess of oil smears the wall of a container (Fig. 1). This will take place within one or two drops of oil. It is important that there is no rubbing or grinding when this test is carried out. Although the current test calls for use of a steel spatula with particular dimensions and a glass flask for the test, variations of these tools have been used [*13,14*].

Oil Absorption, A, is expressed as grams of oil per 100 g of pigment and is calculated as follows

$$A = \left[\frac{M \times 0.93}{P}\right] \times 100$$

where M is the mL of oil used, P is the amount of pigment used in grams, and 0.93 is a constant that represents the density of the linseed oil. Test results by a single operator and between operators in different laboratories that differ by more than 9.9 and 15.3%, respectively, are suspect. Oil ab-

*This chapter is an abridged and modified version of the chapter with the same title found in the previous edition of this manual [*1*].

[1]Senior consultant, Consolidated Research, Inc., 1513 Brentwood Road, Charleston, WV 25314-2307.

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TABLE 1—Various non-ASTM methods for determination of oil absorption values.

Method	Comment	Reference
Azam	Method same as ASTM D 281 except end point is where paste just adheres to the spatula. See text.	15
Bessey-Lammiman	An indirect method. Pore volume of a compressed pigment wafer is determined. From this, an oil adsorption number is calculated.	8
British Standards Institution	Method is similar to ASTM D 281, but differs mainly in acid value of oil, 7.5–8.5; rubbing is done for 20–25 min.	16
Density End Point	Assumes density of pigment and oil are additive. Can have void volume errors associated with it.	17
National Lead Company	Method is similar to ASTM D 281 and Azam methods, but an attempt is made to regulate rubbing pressure and contact area of spatula and rubbing plate.	18
Smith-Stead	Pigment is added to oil in this method, and a mechanical muller is used to better define the rubbing effort.	19

sorption values obtained by this method and the following rub-out method are given in Table 2.

Spatula Rub-Out Method

ASTM D 281: Test Method for Oil Absorption of Pigments by Spatula Rub-Out [*12*] is another classical test that was first published by ASTM in 1928 and updated from time to time with the latest reapproval in 1989. It is approved for use by agencies of the U.S. Department of Defense. In this test, a stiff, putty-like paste is formed by adding linseed oil in a drop-wise manner to the pigment while it is being thoroughly rubbed with a spatula. It differs from the prior method in that ASTM D 1483 requires only gentle folding and stirring, whereas the rub-out test requires a thorough rubbing action of the pigment and oil with a steel spatula.

Raw linseed oil that meets ASTM D 234 but with an acid number of 3 ± 1 is slowly added in a drop wise manner to a known amount of pigment. After the addition of each drop of oil, the oil is incorporated into the pigment by working or rubbing the two together with the spatula. The end point is taken to be the point where sufficient oil has been incorporated into the pigment to produce a very stiff, putty-like paste that does not break up. Various stages in the spatula rub-out test are described in Fig. 2. The weight of oil is determined, and the oil adsorption value is calculated as the grams of oil used per 100 g of pigment. Test results by a single operator and between operators in different laboratories that differ by more than 14.3 and 38.0%, respectively, are suspect. Oil absorption values obtained by this test and the above Gardner-Coleman test are given in Table 2.

Azam Method

The Azam Method [*15*] is essentially the same test as ASTM D 281 with the main difference being a more rigorously defined end point. The end point is defined as the point where the paste just adheres to the spatula and the paste was termed a "complete" paste. Azam found that a complete paste absorbed no more oil when immerse in oil, but an "incomplete" paste would absorb oil in an amount sufficient to make it a "complete" paste. The end point check was made by immersing the rub-out mass in a known amount of oil and then determining the change after two or three days.

PLASTICIZER ABSORPTION BY PIGMENTS

Although linseed oil is used to obtain the oil absorption values, it is obvious that a variety of liquids can be absorbed by pigments. Typical data for selected plasticizers as well as raw linseed oil are given in Table 3.

CRITICAL PIGMENT VOLUME

For a long time, the paint industry formulated on a weight basis. In 1926 Calbeck [*20*] concluded from a statistical study of house-paint test results that the pigment/binder system should contain at least 28 vol% pigment. Not long after this, Wolff [*21,22*] related optimum performance of exterior paints to their critical oil contents, and simple graphical methods for determining this parameter were devised [*23*]. When Elm [*24*] investigated this concept, he confirmed Wolff's findings, but found it necessary to reverse the point of reference so it expressed the critical composition in terms of pigment content as in the work of Calbeck. Later Vannoy [*25*] studied the matter and concluded that replacement of certain pigments by others on a volume basis was the manner in which formulating should be approached. From such studies, the relationship known as the pigment volume concentration (PVC) came into use. It is a simple percentage calculated in the following manner:

$$\text{PVC} = \left[\frac{\text{Pigment Volume}}{\text{Pigment Volume} + \text{Vehicle Solids Volume}}\right][100\%]$$

Studies such as these led to the critical pigment volume concentration (CPVC) concept, and its importance to paint formulation was established by Asbeck and Van Loo [*26*]. When there is just sufficient binder present to fill the voids between pigment particles in the dry paint, the paint is said to be at the CPVC. This is the point of commonality at which a variety of properties show marked change. These properties include corrosion resistance as evidenced by blistering and rusting, ease of stain removal, gloss, hiding, scrub resistance or washability, water-vapor permeability, as well as others.

For example, it is readily understood that gloss decreases as pigment volume increases, that permeability and rusting are relatively constant until the pigment concentration reaches relatively high values after which marked decreases

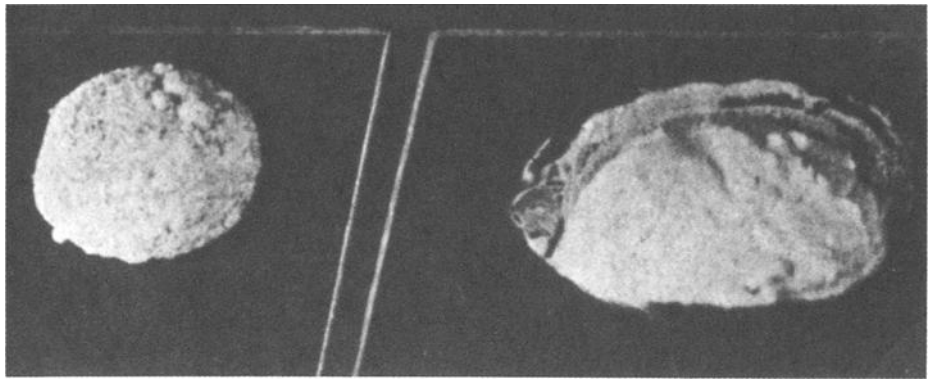

FIG. 1 [*1*]–Critical states in the Gardner-Coleman test. Left photograph is the oil/pigment mass just before the end point where the mass retains its rigidity. The right photograph is the mixture at the end point where the mass undergoes slight flow and smears the glass.

TABLE 2—Oil absorption values, grams of oil/100 g of pigment, of some common pigments [*1*].

Pigment	Gardner-Coleman Test	Spatula Rub-Out Test
Barytes	13.5	...
Basic carbonate of white lead	18	13.0
Basic sulfate of white lead	30	12.8
Blanc fixe	30	15.0
China clay	51	30.0
Gypsum	33.5	...
Lithopone	33	21.5
Silica, crystalline	23	...
Silica, amorphous	32	29.0
Talc	60	...
Titanox	26	18.5
Whiting	32	17.5
Zinc oxide	52	19.5

in performance takes place, and so on. It is at the CPVC that the marked changes take place. When two vehicles—latex, oil-base, etc.—are compared in a given formulation, one may have a higher CPVC than the other. Predictably, the one with a higher CPVC formulation should have better permeability characteristics, such as stain and scrubbability, than the other. Pigment or vehicle could be added to one paint or the other, and a paint with comparable properties can be prepared. The selection of which paint to modify by increasing pigment or vehicle is made on the basis of additive economics.

Different end-use requirements impose different pigment volume concentrations that are above or below the CPVC. For example, a ceiling paint does not need to have excellent washability, and usually this paint type only requires low to moderate gloss. Therefore, a paint such as this can be formulated at or even above the CPVC. In contrast, many exterior paints that have a high gloss as well as glossy enamels are formulated well below the CPVC, and it is PVC rather than CPVC that has significance. Although the parameter was devised for oil-based paints, the concepts involved are important to other types of coatings.

The pigment volume is often expressed as bulk, which is the volume occupied by a given weight of pigment. It is calculated by multiplying pigment specific gravity by the weight of a gallon of water or 8.33 (1 kg/L). For example, if a pigment has a specific gravity of 2.0, its bulk can be calculated as follows

$$\text{BULK} = \left[\frac{2.0\ \text{g/cc}}{1.0\ \text{g/cc}}\right]\left[\frac{8.33\ \text{lb}}{\text{gal}}\right] = \frac{16.66\ \text{lb}}{\text{gallon}} = \frac{2.0\ \text{kg}}{\text{litre}}$$

Since the paint industry is usually interested in gallons of product, the bulk is often expressed as the reciprocal of this number or 0.06 gal/lb (0.5 L/kg) or as bulk per 100 lb, 100/16.66 = 6.00 gal/100 lb in this example. From this example, it is apparent that the higher the bulking value of a pigment, the more advantageous it is from a cost standpoint. If pigment is lower in cost than vehicle, and assuming equivalent performance, a pigment with a higher bulking value over another would be selected.

Asbeck-Van Loo Method of Determining CPVC

The Asbeck-Van Loo [*9,26*] method of directly determining the CPVC is based on the observation that the packing pattern of a pigment in a paste persists when the dispersion is diluted for sedimentation tests if nonpolar liquids are used for the dilutions. Thus, to measure the voids in a dry paint film, it is only necessary to obtain the pigment in the form of a filter cake and measure the volume of the cake. Then, the cake volume is subtracted from the actual volume of the pigment calculated from density data. The ratio of the actual volume of the pigment to the volume of the cake is the CPVC.

Pigment Packing Factor

Asbeck and coworkers [*9*] proposed the term "pigment packing factor" (PPF) as a name for a pigment parameter that replaces or supplements the oil absorption value. PPF is the CPVC for a single pigment in a standard vehicle with the term CPVC being applied to a single or mixture of pigments present in a paint. The investigators suggested a blend of 4 mL of heat-bodied linseed oil and 50 mL of naphtha as the dispersing vehicle. The PPF is determined by placing 54 mL of the vehicle in a ¼-pt can or glass jar that is half filled with steel balls. To this, 6 mL of pigment (the weight in grams of pigment equal to the specific gravity times 6) are added. The system is dispersed by machine shaking for exactly 3 min.

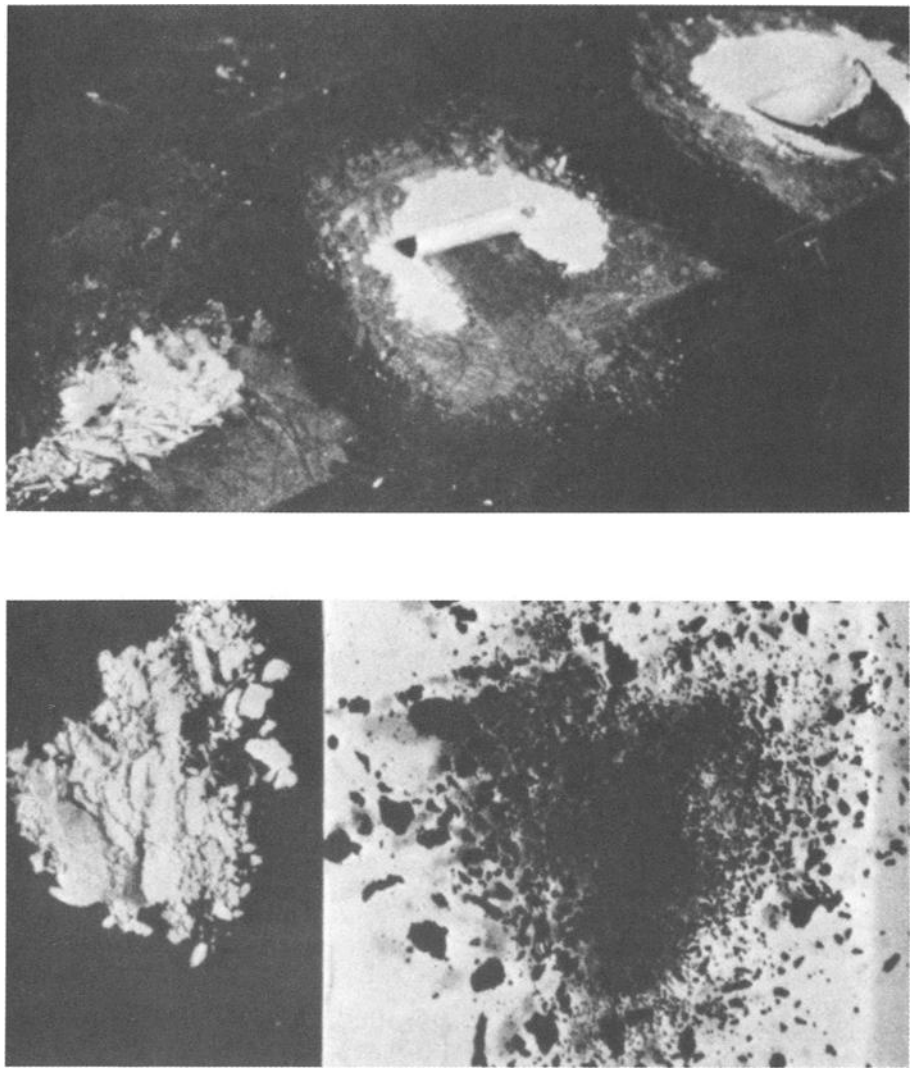

FIG. 2 [*1*]–A, B, and C in the top photograph represent 1 g of zinc oxide that has been mixed with increasing amounts of linseed oil. Rub-Out A (top) is crumbly and breaks up when an attempt is made to lift it with a spatula. Rub-Out B (lower left) is coherent and tends to form a roll when deformed with the spatula. Rub-Out C (lower right) contains too much oil and does not roll. It can be lifted as a sheet and the mixture is beyond the end point. The bottom two photographs are additional examples of the mixture condition just before the end point is reached. A single drop of oil will convert the crumblings into coherent masses.

Twenty millilitres of the dispersion are then used to determine the PPF using the same procedure as that used for CPVC. If the PPF is to be compared with oil absorption values, it must be converted to a weight basis, PPF_{weight}, by means of

$$PPF_{weight} = \left[\frac{(100 - PPF)(\text{specific gravity of oil})}{(PPF)(\text{specific gravity of pigment})}\right](100)$$

Cole Method for CPVC

The CPVC depends on pigment particle packing or orientation [*9,26*], and Cole [*27*] noted that spherical particles may pack similarly in both liquid and dry films. To demonstrate this, a dry-film method was developed. The method is based on the fact that below the CPVC dry film volume, V, is a sum of the pigment, V_p, and binder solids, V_b volumes

$$V = V_p + V_b$$

and that above the CPVC the volume of the voids must also be considered with

$$V = PV_p$$

where P is the relative pigment packing factor (the ratio of bulk volume to true volume). Two graphical and calculation methods were used to obtain CPVC.

Pierce-Holsworth Method for CPVC

This method [*28*] also used paint films, but it treated the data in a different manner by introducing specific volume

TABLE 3—Plasticizer absorption for some typical pigments [*1*].

Pigment	Absorption, g, Plasticizer/100 g Pigment		
	Tricresyl Phosphate	Dibutyl Phthalate	Raw Linseed Oil
Barium titanox	27.6	24.2	17.0
Carbon black, super	179.0	147.0	106.0
Calcium titanox	37.2	39.4	22.0
CP cadmium red	26.0	26.2	14.0
CP cadmium yellow	48.4	50.5	37.2
CP Chinese blue	145.0	136.5	41.1
CP chromium oxide	29.5	24.7	17.0
CP chrome orange, medium	19.5	21.0	7.5
CP glen green DD	78.0	72.5	28.9
Chromium hydroxide, green	80.0	76.6	53.0
Lampblack	118.0	126.0	145.0
Lithol toner	65.0	50.5	50.0
Lithopone, high strength	35.4	32.5	24.0
Madder Lake	106.0	81.0	51.4
Titanium dioxide	54.3	47.2	22.5
Toluidine red	31.9	20.0	35.0
Ultramarine blue	65.0	55.0	31.6
Zinc Oxide	28.3	25.2	14.5
Zinc Sulfide	37.2	34.1	15.7

concepts. The specific volume, v, of a dry paint film can be expressed as

$$v = \frac{V}{W} = \frac{V}{W_p + W_b} = v_p f_p + v_b f_b$$

where V is the dry film volume, v, v_p, and v_b are specific volumes of the dry film, pigment, and binder; W, W_p, and W_b are weights of dry film, pigment, and binder; and f_p and f_b are weight fractions of pigment and binder, respectively. Since the sum of f_p and f_b is unity, the expression can be arranged to

$$v = (v_p - v_b)f_p + v_b$$

If v is plotted as a function of f_p, a straight line of slope $(v_p - v_b)$ and intercept of v_b should result.

Above the CPVC, the volume of the film is given by

$$V = Pv_pW_p$$

where P is a packing factor. If both sides of this expression are divided by W, the expression

$$v = Pv_pf_p$$

is obtained. If dry film specific volume, v, is plotted against the weight fraction of pigment, f_p, a straight line of slope Pv_p passing through the origin results. The intersection of this line with the previously described straight line should occur at a value of f_p corresponding to the CPVC. Results obtained by this method are presented in Table 4 along with the CPVCs obtained by tensile strength, elongation, and water vapor permeability. The good agreement is apparent.

A number of papers detailing studies of CPVC and its importance [*29–34*] as well as information relating CPVC, OA, and viscosity [*35,36*] can be found in the literature.

CRITICAL PIGMENT VOLUME CONCENTRATION AND OIL ABSORPTION

Oil absorption and CPVC are accepted to be interrelated [*29–31*] and actually are two ways of stating the same concept: i.e., CPVC is the concentration of pigment in a pigment-binder system that contains just sufficient binder (oil) to fill the space between the pigment particles [*1*]. If the parameters are to be equated, it is necessary to determine the oil absorption value (*OA*) by the spatula method and to express the results in volume terms. If *OA* is expressed as X volumes of oil per Y volumes of pigment, then

$$\text{CPVC} = \frac{Y}{X + Y}$$

When *OA* is expressed as the fraction X/Y and Y is set to one, then $X/Y = X$ and

$$OA = \frac{\text{CPVC}}{1 - \text{CPVC}}$$

and

$$\text{CPVC} = \frac{1}{1 + OA}$$

The PPF and *OA* values are compared in Table 5. If values are ranked from highest to lowest, the values calculated from the PPF are highest, those from Gardner-Coleman fall next, and those from the spatula rub-out test are lowest. Explanations [*1,9*] for the difference based on conditions existing at the end point are tabulated in Table 6.

Investigation of the effect of pigmentation on selected properties of flat wall paints has indicated that optimum levels of pigment concentration for color uniformity and enamel holdout corresponded to the CPVC [*32,33*]. In addition, the study indicated that rub-out *OA* values are a good indication of the CPVC. Stieg [*31*] points out that any one

TABLE 4—[*1*] Comparison of the critical pigment volume concentration calculated by the Pierce-Holsworth method [*28*] and comparison with results from physical property measurements.

Paint System	Critical Pigment Volume Concentration			
	Pierce-Holsworth Method	Tensile Strength Method	Elongation at Break Results	Water Vapor Permeability Results
Acrylic latex exterior House Paint A	47	47	42	46
Acrylic latex exterior House Paint B	41	42	41	42
Poly(vinyl Acetate) latex masonry paint	44	44	44	45
Acrylic exterior masonry paint (from House Paint A above)	48	47	44	48

TABLE 5—Comparison of pigment packing factors, calculated and experimentally determined oil absorption values [*1*].

Pigment	PPF	Oil Absorption Values		
		Calculated from PPF	Gardner-Coleman Method	Spatula Rub-Out Method
Carbon black, medium	10	456	212	124
Chrome green	34	41	33	20
Chrome yellow	27	46	33	24
Iron oxide, light red	37	32	24	19
Lampblack	29	128	70	51
Magnesium silicate	39	50	27	25
Midori blue	33	104	87	51
Phthalocyanine blue	20	225	55	34
Silica, diatomaceous	24	131	105	65
Toluidine red toner B	25	199	62	48
Zinc oxide	27	45	19	12

operator of the spatula rub-out test can reproduce personal test results with a reasonable degree of accuracy. It seems that interpretation of the end point and not reproducibility is the source of variation between operators in these tests. Oil adsorption of pigment mixtures has been treated by Armstrong and Madson [*37*].

CHARACTERIZATION OF DISPERSIONS AT THE OIL ABSORPTION POINT

Examination of the dispersions (pastes) formed between oil and pigment at the oil absorption point is a source of considerable information. Large differences exist in such pastes with some being long, stringy, and soft in character. Others are tough and short, others have a high gloss, others have a dull appearance, others are soft and easy to spread, and still others are stiff and require a large pressure spread or flatten. The amount of oil needed is not closely related to these attributes, and one is led to the conclusion that pigments with essentially the same oil absorption value can yield pastes with markedly different character.

Daniel and Goldman [*38*] developed a scheme for evaluating dispersion character by using the paste obtained at the end of the spatula rub-out test. The amount of liquid needed to wet the pigment and produce flow are determined. From this information and the types of flow exhibited by the pastes, dispersions are classed as good, fair, or poor. From 10 to 20 g of dispersion is worked with a fairly stiff steel spatula in the test. The oil absorption value is called the *wet point*. From this point, oil addition is continued until the *flow point* is reached. In well-dispersed systems, the flow point is the stage where a substantial portion of the paste flows from a vertically held spatula without leaving jagged flow edges. In poorly dispersed or flocculated systems, the flow point is the stage where the paste drops from a vertically held spatula. Cases intermediate to these two are difficult to define. At the instant when paste drops from the spatula, it elongates at the edge. If a paste does not flow after addition of 10 to 20% more liquid than is required for the wet point, a portion of the diluted paste is placed on the tip of a horizontally held spatula. The spatula is then tapped near the handle with a finger. The tapping is gentle at first and then more vigorous. The paste

TABLE 6—Physical conditions that exist at the end points of pigment packing factor and oil absorption test [*1,9*].

Parameter	PPF	Gardner-Coleman	Spatula Rub-Out
Dispersion	Aggregates are completely broken down.	Only a few of the largest aggregates are broken down and the interstices are filled with oil.	More aggregates are broken down than in the Gardner-Coleman methods and the interstices are filled with oil.
Electrokinetic equilibrium	Agglomeration is complete because of high system fluidity.	Agglomeration is incomplete because of low system fluidity.	Agglomeration is incomplete because of low system fluidity.
Pigment surface requirements	Satisfied	Not completely satisfied	Substantially satisfied
Work of dispersion	Defined and very high (approaching maximum)	Undefined but low	Undefined but relatively high
Work of packing	Defined and very low (approaching zero)	Undefined but low	Undefined but relatively high

TABLE 7—Characteristics of pastes from oil absorption studies [*1*].

Observation Point	Good Dispersion	Fair Dispersion	Poor Dispersion
At wet point	Shines without tapping or with light tapping; dry and difficult to knead	Shines when sharply tapped	Remains dull even when sharply tapped
At intermediate stage	...	Flows only on tapping; occasionally has a resistance to suddenly applied pressure	Rises on tapping; has no resistance to suddenly applied pressure; has a high yield value
At flow point	Flows without tapping; offers resistance to suddenly applied pressure	Falls with elongation at breaking line; no resistance to suddenly applied pressure; has visible thixotropy	Falls without elongation at breaking line
Gap between wet and flow points	Very small	...	Very large

may then become glossy and flow over the edge of the spatula, in which case it is passively dilatent, or it may tend to rise or otherwise decrease the interface between it and the blade, in which case it is flocculated. Characteristics of pastes tested in this manner are given in Table 7. A test such as this can yield practical rheological results without sophisticated testing equipment.

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Part 7: Additives

29

Bactericides, Fungicides, and Algicides

by Vanja M. King[1]

THE VARIED METABOLIC CAPABILITIES of microorganisms enable them to cause many problems in paints and coatings, from manufacture through storage and application. These problems can usually be controlled with the effective use of microbicides (bactericides, fungicides, and algicides). The organisms involved are also discussed elsewhere in this manual. Knowing the type of organisms against which a microbicide is to provide protection is very important in selecting the best types of chemicals to use.

Other considerations in the selection of the treatment chemicals include the intended application of the end product, the composition of the product being preserved, and the desired level of performance. The physical parameters are also of great importance. Some types of organics and inorganics, pH levels, temperature at the time of addition, and ultraviolet (UV) exposure of the film may deactivate the biocide used [*1,2*]. A thorough knowledge of the biocides available will help the chemist select the proper materials for his or her system and help minimize the occurrence of unpleasant surprises.

Environmental considerations and public opinion are also of great importance. Strong feelings have evolved about antimicrobials like mercury and tin. Some toxicological concerns regarding biocides are: exposure during manufacturing, storage, application, clean up (washing), and disposal of wash waters.

Definition of Terms

Following are definitions of the terms used:

- A *biocide* is a substance that kills organisms. The use in this section is synonymous with microbicide. Occasionally the terms are further defined (bactericide, fungicide, algicide) to include the types of organisms killed.
- A *microbiostatic* agent is one that prevents the growth of microorganisms and their spores, but does not necessarily kill them.
- A *preservative* is an agent that slows down the biodeterioration of a material. (An important factor to remember is that bacterial endospores only need to be kept from germination and outgrowth because endospores are nonmetabolizing and cannot cause deterioration or spoilage.)
- *Toxicity* is the deleterious effect on organisms other than the target organism. Aquatic toxicity of a fungicide would be an example of a fungicide's effect on fish, etc.
- *Efficacy* is the effect of a microbicide on the target organism or group of organisms. Efficacy could be measured in percent kill compared to control, but should be defined in the test method. The result is usually expressed as the minimum inhibitory concentration (MIC) against a specific organism.
- *Colonization* refers to the establishment of growth of organisms on a surface.
- *Spectrum* is a term describing the efficacy of a microbicide; *broad spectrum* means that the microbicide is effective against more than one group of microorganisms.
- *Microbial pigments* refers to colored substances produced by microorganisms. These include both water-soluble and water-insoluble compounds.

DESCRIPTION OF MICROBIAL PROBLEMS

In-can Preservation

Problems frequently associated with unpreserved, water-based paints have increased in recent years, mainly because water-based paints have become much more common. These formulations are susceptible to attack by bacteria and unicellular fungi (yeasts) and occasionally filamentous fungi. There are several food sources available for growth of microorganisms in common coatings formulations; cellulosic thickeners, surfactants, and defoamers are all molecules used as a carbon source by microorganisms. Good discussions can be found in Refs *3–5*. The problems most commonly encountered in water-based paints include those shown in Table 1.

To prevent these problems from occurring, an effective biocide should be incorporated into the coating. It must be cost effective, be compatible with coating ingredients, impart no color to the formulation, have no objectionable odor, be nonyellowing in the dried film, and be environmentally acceptable in manufacture, handling, and release into the environment.

The best understood problem in coating film preservation is the disfiguring growth of organisms on the exterior surface of the film itself [*6,7*], such as on ships, bridges, and interior and exterior walls of buildings. Less understood are problems associated with loss of adhesion from fungi growing underneath the coating film and the corrosion problems on equip-

[1]Chief research microbiologist, Buckman Laboratories International, Inc., 1256 N. McLean Blvd., Memphis, TN 38108.

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TABLE 1—Problems caused by contamination of water-based paints.

Type of Problem	Common Cause
Gassing—swelling or exploding cans	CO_2 released by bacteria or yeasts.
Viscosity loss	Cellulase enzymes produced by bacteria or fungi attacking thickeners.
Odors	Organic acids and other metabolic byproducts of microbial metabolism.
pH change/physical instability	Organic acids produced can lower pH of paint.
Loss of paint film fungicide/algicide	*Pseudomonas* sp. bacteria are well known for detoxifying antimicrobials; *Cladosporium resinae* is reported to deactivate methylparaben.
Gelation	*Pseudomonas* sp. have been implicated.
Discoloration	Both bacteri and fungi/yeasts growing in and on in-can materials can produce water-soluble and insoluble pigments.
Slime formation	Biofilm formation by slime-forming bacteria and fungi can produce clumps in the liquid and slime on the sides of pipes and cans.

ment from the moisture produced by the respiration of fungi. Fungicides are needed to control these problems.

There is a continuing need for sanitizing and disinfecting paint films. In this case, there is more need for a bactericide than a fungicide. For example, the hospital environment continues to be conducive to so-called nosocomial infections (those acquired in the hospital) and, with the rise in numbers of immunocompromised and elderly patients, paints containing long-lasting bactericides are needed. Many compounds may not remain active the length of time needed for them to work.

Microbicide toxicity and efficacy are often concerns when preserving coating films. Fungicides and algicides are frequently more toxic than most common bactericides since fungal and algal cells share many similarities with cells from higher organisms, while bacterial cells are distinctly different. Most microbicides are limited to efficacy against one group, and some of the more effective antimicrobials target specific metabolic pathways unique to one group of organisms.

Several recent studied [*8,9*] have shown a relationship between bacterial growth, their polysaccharides, and subsequent colonization of surfaces by fungi or other organisms. It appears that colonization succession occurring on dry films is similar to that occurring on ship bottoms. This implies that there should be a bactericide *and* a fungicide incorporated for coating film protection. Some biocides can provide both functions. In tropical climates, disfiguring growth of algae on the exterior of the films is also a problem [*10,11*]. Table 2 indicates problems in paint and coating film preservation.

TABLE 2—Problems in paint and coating film preservation.

Type of Problem	Common Cause
Discoloration/dirt entrapment	Algae and/or fungi.
Loss of adhesion	Fungi.
Corrosion	Moisture produced by fungi.
Need for sanitizing agents in film	Microorganisms on hospital walls.
Antifouling paints on marine crafts and structures	Bacteria, fungi, algae, barnacles, hydroids, etc.
Production of growth promoting substances	Algae and fungi.
Destruction of cultural objects	Algae, fungi, and bacteria growing on paintings, statues, and buildings.

GROUPS OF MICROORGANISMS RELATED TO BIOCIDAL EFFICACY

It is important to know the activity of a particular preservative/biocide against the types of organisms encountered by the formulation. For this purpose, the most important groups of microorganisms are:

Bacteria

Aerobic bacteria
- Gram positive bacteria
  - endosporeforming bacteria
- Gram negative bacteria

Anaerobic bacteria
- Gram positive bacteria
  - endosporeforming bacteria
- Gram negative bacteria

Fungi

Multicellular (molds)
Unicellular (yeasts)

Algae

Green algae
Blue-green algae (cyanobacteria)

NOTE: All of these organisms are described in more detail elsewhere.

MODE OF ACTION OF MICROBICIDES/ SPECTRUM OF ACTIVITY

It is very important to note the difference in the activity of a particular biocide against the different organisms within a group, and differences are to be expected. The most important consideration is to know which organisms one is trying to protect against and to use an effective agent. When the mode of action of a biocide has been elucidated, it frequently explains the differences in activity. The lists below are not meant to be comprehensive. They describe some materials well known to the industry and report on the organisms against which the compounds are most effective [*12–14*].

Another important factor related to the spectrum of activity is concentration. Some biocides are effective against bacteria in one concentration and effective against fungi in a much higher concentration; the reverse can also be true. Furthermore, a biocide may be microbiostatic in a low concentration and microbicidal in another. The general definition of "microbiostatic" is that it interferes with some activity of the organisms without necessarily killing them. A "-cidal" compound kills the organisms. The definition of a microbiostatic/microbicidal compound is here broadened to include concentration. The underlying principles to the mode of action are generally agreed upon to be one of two mechanisms:

1. Membrane-active compounds such as quaternary compounds.
2. Electrophilic agents (react with nucleophilic groups on or within cells).

Table 3 shows some metal microbicides used in paints and coatings.

Because of environmental concerns, the use of many heavy-metal-containing biocides traditionally incorporated in coatings has become more limited [*15*]. An example is the recent (1988) ruling by the EPA regarding the maximum release of tributyl tin. The Organotin Antifouling Paint Control Act essentially restricts the use of organotin antifouling paints to commercial and military crafts. In 1990, the U.K. revoked the use of tributyl-tinoxide (TBTO) in surface biocides for professional and amateur use. Mercury-type compounds are losing favor with a large segment of the coatings industry and the public, and it appears likely their use will continue to decrease as nonmercurials replace them in the future. The toxicity of some mercurial compounds, notably methyl mercury, also makes them very potent and long lasting preservatives with a broad spectrum of activity.

Some positive effects of the metal compounds on the properties of coatings should also be noted. Barium metaborate, a pigment, has been reported [*2*] to act as a corrosion inhibitor and a UV light stabilizer. Zinc oxide further enhances drying of the paint film (which is a desirable property) and makes it more resistant to fungi [*12*]. Table 4 shows some nitrogen and/or sulfur-containing microbicides used in paints and coatings.

For an excellent summary of the chemistry of many of the compounds shown in Table 4, please see Ref *16*.

Table 5 indicates some nitrogen and/or sulfur-containing microbiocides used in paints and coatings. Many of the biocides listed in Table 5 are important to this industry, especially from a general housekeeping standpoint. The importance of cleanliness in the production of all types of materials should be emphasized since heavy contamination of a product is difficult to overcome with any preservative. Disinfection of pipes and vessels along with a general washup will remove the surviving, more resistant organisms.

MODE OF ACTION OF SOME ANTIMICROBIAL AGENTS

The following is not intended to explain all possible modes of action, but to give a general overview of the terms used in the biocide listings. More detailed explanations can be found in the references listed at the end of this chapter.

Agents that React with Acetylacetone

This term describes chemicals that, when treated with acetylacetone (Nash's reagent), will yield formaldehyde. Some of these act as preservatives by releasing formaldehyde, while others (manufactured through condensation reactions with a starting compound and formaldehyde) may not necessarily act through the release of formaldehyde. The release of formaldehyde is also related to pH. At alkaline pH, little or no formaldehyde is released.

Formaldehyde interacts with amine groups on proteins in a condensation reaction, thereby deactivating them. Proteins are common on the outer layers of microorganisms and many also produce extracellular proteins (enzymes) for metabolism of large molecules like cellulose. Deactivated proteins hinder metabolism or growth or may actually kill the organism. A common result is the leakage of the contents of the cell into the environment.

Because of the current public unease concerning formaldehyde, few biocide producers like to call their products formaldehyde releasers. However, this is probably the most common mode of action among the bactericides. It is very

TABLE 3—Some metal microbicides used in paints and coatings.

Composition	Effective Against	Putative Mode of Action
Barium metaborate	Broad spectrum	Enzyme inhibition
Copper (II) 8-quinolinolate	Fungi	General coagulation
Phenylmercuric acetate and other organo-mercurials	Broad spectrum	Protein deactivation (coagulation), etc.
Tributyl tin oxide and other tributyl tins	Broad spectrum, except gram negative bacteria	Chelation, enzyme inhibition
Zinc oxide	Fungi, algae	Chelation, protein inhibition
Zinc-dimethyl dithiocarbamate + Zn_2-mercaptobenzothiazole	Fungi	Chelation of necessary metals; possibly interferes with oxidative phosphorylation
Zinc 2-pyridinethiol-N-oxide	Fungi	Chelation of necessary metals

TABLE 4—Some nitrogen and/or sulfur-containing microbicides used in paints and coatings.

Composition	Effective Against	Putative Mode of Action
4,4-dimethyl-oxazolidine + 3,4,4-trimethyloxazolidine	Bacteria	Reacts with acetylacetone
5-hydroxy-methyl-1-aza-3,7-dioxabicyclo (3.3.0.) octane*	Bacteria	Reacts with acetylacetone
2(hydroxymethyl)-aminoethanol	Bacteria	Inhibits active transport; coagulates protein
2[(hydroxymethyl)-amino]-2-methyl-1-propanol	Bacteria	Reacts with acetylacetone
Methylenebis(thiocyanate)	Bacteria/fungi/algae	Attacks cellular thiols; inhibits oxidative phosphorylation
1,2-dibromo-2,4-dicyanobutane	Bacteria/fungi/algae	Has several highly electron withdrawing centers
2-(4-thiazolyl)benzimidazole	Fungi	*Low:* inhibits ergosterol synthesis *High:* membrane damage; interacts with DNA synthesis; blocks oxidative phosphorylation
2-mercaptobenzo-thiazole	Fungi/bacteria (?)	Chelation of necessary metals
1,2-benzisothiazoline-3-one	Bacteria/fungi/yeast	Interacts with nucleophilic components
5-chloro-2-methyl-3(2H)-isothiazoline + 2-methyl-3(2H)-isothiazolone	Fungi/bacteria Bacteria	At physiological pH, reacts oxidatively with thiol-containing compounds; thio-acyl chloride formation
4-(2-nitrobutyl)-morpholine + 4,4′-(2-ethylnitrotrimethylene dimorpholine	Fungi/bacteria	Interferes with membrane synthesis (fungi); ergosterol synthesis
Zinc 2-pyridinethiol-N-oxide*	Fungi	Chelation of necessary metals
Tetra-hydro-3,5-di-methyl-2H-1,3,5-thiadiazine-2-thione	Bacteria/fungi	Detected with acetylacetone
N-trichloromethyl-thio-4-cyclohexene-1,2-dicarboximide	Fungi	Reacts with thiols = disulfide; inhibits respiration
Hexyhydro-1,3,5-tri-ethyl-s-triazine	Bacteria	Detected with acetylacetone
2-n-octyl-4-isothiazoline-3-one	Fungi	Reacts with thiol-containing compounds
1-(3-chloroallyl)-3,5,7-triaza-1-azonia-adamantane chloride	Bacteria	Detected with acetylacetone
1-methyl-3,5,7-triaza-1-azonia-adamantane chloride	Bacteria	Detected with acetylacetone
2,4,5,6-tetrachloro-isophthalonitrile	Fungi	Reacts with thiols; inhibits oxidation of glucose
3-iodo-2-propynyl butyl carbamate	Fungi	Chelation?
N-(trichloromethyl-thio)phthalimide	Fungi	Reacts with thiols = disulfide; inhibits respiration
2-(thiocyanomethyl-thio)benzothiazole	Fungi/anaerobic; bacteria/algae	Reacts with thiols/inactivation of metal enzyme complexes
Diiodomethyl-p-tolyl sulfone	Fungi	?
Potassium N-hydroxy-methyl-N-methyl-dithiocarbamate	Fungi	Chelates necessary metals
2-(thiocyanomethyl-thio)benzothiazole + methylenebis (thiocyanate)	Bacteria/fungi/algae/anaerobic bacteria/mollusks	Uncouples oxidative phosphorylation; reacts with SH-groups
Sodium 2-pyridinethiol-1-oxide	Fungi	Chelation; ATP; transport; protein synthesis

*Other actives also present in the formulation.

TABLE 5—Some other microbicides used in the coatings industry.

Composition	Reported Effective Against	Putative Mode of Action
Glutaraldehyde	Bacterial spores, bacteria, fungi, algae	Reaction with proteins
Parabens (ethyl, or propyl, methyl, or butyl parahydroxybenzoate)	Fungi	Membrane activity and integrity
Quarternary ammonium compounds	Bacteria, algae	Generalized membrane damage
Chlorine biocides	Broad spectrum	Deactivation of proteins

effective against bacteria, but it is less effective against yeasts and multicellular fungi.

Formaldehyde in its mode of action could also be classed with the electrophilic agents, which are agents that react with nucleophilic components of a cell.

Agents that React with Nucleophilic Groups

Thiols are nucleophilic groups on amino acids (building blocks of proteins) or proteins found in all living cells; some are reducing agents containing S groups. The cytoplasm of cells of all types of organisms contain a pool of amino acids and proteins. Biocides that contain electrophilic groups react with the nucleophilic areas of the cell, and deactivation of the organism occurs.

Such biocides can also react with coating components that contain nucleophilic groups. This results in the loss of some activity commensurate with the concentration of each reactant. Reversal of biocidal activity or deactivation could result from the addition of such materials. As the biocide reacts, it is being used up and unavailable for further activity.

A review of the chemistry of a preservative molecule could reveal one or more electron withdrawing centers that would be able to react with nucleophilic groups. There are many compounds in this category.

Agents that Chelate Metals

Metals are necessary as trace elements for organisms. The metals are frequently parts of enzymes or vitamins needed for growth and metabolism. It is postulated that chemicals that chelate metals would deactivate microorganisms by withdrawing the metals needed for life.

Cationic Agents

Cationic polymerics are frequently used as sanitizing agents. Such molecules would react with anionic constituents, inorganic and organic (such as those present on the surface of the microbial cell wall). The cationic material causes leakage of materials from the cell through the destabilized cell wall, causing death of the cell.

Other Mechanisms

Coagulation is a term denoting a general deactivation of proteins or cells without specifying the molecular action. Interference with active transport (of food molecules into cells) may be from deactivation of transport proteins or by adsorption of molecules onto the cell surface, blocking the transport proteins. Ergosterol is an important lipid component of the fungal membrane, and interference with its synthesis would be fungistatic in low concentrations and fungicidal in high. Inhibition of respiration (oxidative phosphorylation) results in the cell being unable to generate energy (ATP or adenine triphosphate) through metabolism, eventually killing it. Interference with DNA (deoxyribose nucleic acid; chromosome material), RNA (ribose nucleic acid), or protein synthesis would hinder reproduction and metabolism, eventually killing the cell.

STRATEGIES FOR MINIMIZING RESISTANT STRAINS

The topic of resistance to antimicrobials is mentioned frequently in industrial preservation discussions, probably because we are all familiar with resistance of disease-producing microorganisms to therapeutic antibiotics. The issue of resistance seems less obvious when dealing with industrial biocides.

The most important factor for minimizing contamination and resistant strains is general housekeeping. Leaving water in pipes and vessels that previously contained preserved material would provide diluted biocide in nonlethal concentrations to which microorganisms could become resistant.

There are different opinions regarding genetic resistance to disinfectants and antimicrobials. It frequently appears that, when an organism becomes resistant to one biocide (such as quarternary ammonium compounds), it will also be resistant to several, chemically unrelated biocides (such as thiazolinones) [*17*]. This, of course, happens more readily when similar biocides are used (such as formaldehyde releasers). Therefore, changing the biocide may not be the solution to resistant organisms; rather, it may make matters worse by widening the materials to which resistance is observed.

Testing of biocides should utilize organisms isolated from the manufacturing plant and spoiled materials. Plant isolates are almost always more resistant to biocides than stock cultures maintained on artificial media. Also, selection of a good broad spectrum biocide minimizes the possibility of resistant organisms. Finally, a thorough knowledge of the chemistry of available biocides will keep one from using products with similar modes of action consecutively.

ANALYSIS AND DECONTAMINATION

It is of considerable importance to be able to accurately analyze for the presence and concentration of the antimicrobial agent. One reason is the ability to ascertain that the material was, in fact, added and in the right concentration both as a quality control measure parameter and in case of a failure in the field.

Available methods vary with the type of active ingredient utilized. Preferably, the molecule should be determined without employing a destructive method since one could not determine if breakdown had occurred in the container or if breakdown occurred because of the method of analysis. For example, it would be preferable to determine the intact molecule of a formaldehyde releaser rather than determining the formaldehyde present after breaking up the molecule. The formaldehyde release could have occurred before analysis was attempted. Nondestructive methods include NMR (nuclear magnetic resonance) methods.

The information literature on a preservative product frequently contains procedures for deactivation of the biocide. This information is necessary for several reasons. A spill can always occur, and a puddle of chemical would need to be neutralized and cleaned without danger to personnel. In addition, when testing for efficacy of preservatives, small concentrations remaining even after dilution for enumeration may be at microbiostatic levels. If the organisms had not been killed, there is a chance for regrowth and spoilage. A method for neutralizing the biocide should, therefore, always be used in the growth medium when performing preservative efficacy tests.

FACTORS THAT IMPACT THE EFFICACY OF SOME COMMON ANTIMICROBIAL AGENTS

The importance of physical and chemical factors on the growth of microorganisms is discussed elsewhere; however, many of the same factors are also important because of their impact on the activity of biocides. The impact is frequently detrimental [*18*], but can also be positive. Some factors are described in Tables 6 and 7.

TABLE 6—Factors that positively influence biocide efficacy.

Inclusion of pigments that have antimicrobial activity.	Such components could possibly cut down on the amount of preservative needed.
Inclusion of other materials in the formulation that have antimicrobial activity (e.g., propylene glycol) or resist degradation	Some components are less readily used as a food source (e.g., choices of carboxymethylcelluloses).
Many biocides are more effective at acid pH, while others are more active at an alkaline pH.	Adjusting the pH to suit the biocide, if no effects are seen in the formulation, could be helpful.
Difference in solubility of different biocides.	Combining biocides with different solubilities may increase efficacy. An example of this is to use several different parabens, each of which has its own independent solubility.
Synergism resulting from combining biocides with different spectra of activity.	This effect, in most cases, appears to be additive instead of true synergism (when the whole is more than the individual components together). Whichever case, antimicrobial agents are frequently complemented by combination, e.g., the isothiazolones and methylene bis(thiocyanate)/2-(thiocyanomethylthio)benzothiazole).

TABLE 7—Factors that decrease biocidal efficacy.

pH	Knowledge of the chemistry of a biocide should include its activity at different pHs. It is easier to find a biocide that is effective and stable at acid pH than at alkaline, but many are described as being alkaline stable/effective. However, many are considerably less effective at alkaline pH, making an increased concentration necessary. Stability is not to be equated with efficacy since a biocide that is stable at alkaline pH (such as many dithiocarbamates) may not have much efficacy at alkaline pH, except after a long period of time.
Addition temperature	Examples of biocides affected by addition temperatures are the parabens, which need to be added at temperatures below 50°C. It is typical of biocides that they are deactivated to various degrees based on temperature, although this temperature effect varies considerably from biocide to biocide. Increased concentration may alleviate this problem. Typically, increase in pH and increase in temperature is synergistic in deactivating sensitive biocides.
Nonionic surfactants	Biocides that are deactivated by these include the parabens, phenolics, organic acids, and aromatic alcohols.
Low solubility	Preservatives need to be water-soluble to the concentration needed for efficacy. This means that the solubility should not be too high, or that a combination of a soluble and less soluble agent would be most effective.
Leachability	A coating film preservative must maintain an effective concentration within the film to remain antimicrobial. Water-soluble materials would be quickly compromised in this situation. However, some movement may be necessary to transport the antimicrobial through dirt layers that accumulate. This balance may be hard to maintain.
Can components	Can components could adsorb the antimicrobial agent from the content.
Formulation components	Formulation components could deactivate the biocide. Such components are proteins for formaldehyde releasers and thiols for electron withdrawing biocides.
Stabilizing agents	Inclusion of components may keep other biocides from yellowing the film. Sodium sulfite reportedly decreases the chance of 1-(3-chloroallyl)-3,5,7-triaza-1-azonia-adamantane chloride yellowing the paint film. However, such components may deactivate biocides since they are frequently listed as neutralizing materials in preservative brochures.
UV light frequency	UV light frequency decomposes coating film fungicides and algicides. The photolysis products are less effective and efficacy is lost. The inclusion of products that make the film more UV stable alleviates this problem.

METHODS FOR DETERMINATION OF BIOCIDE EFFICACY

There are numerous methods described in the literature for determining the efficacy of a proposed biocide, both for in-can preservation and for paint film use. The appropriate ASTM methods are: D 2574-86, Test Method for Resistance of Emulsion Paints in the Container to Attack by Microorganisms; D 3273-86, Test Method for Resistance to Growth of Mold on the Surface of Interior Coatings in an Environmental Chamber; and D 3456-86, Practice for Determining by Exterior Exposure Tests the Susceptibility of Paint Films to Microbiological Attack. These methods are contained in Section III, "Microbiological Contamination and Biodeterioration Assessment," of *ASTM Standards on Materials and Environmental Microbiology*, first edition, 1987 [*19*]. Several other methods in this section are also of interest. A complete fungicide testing program is described in Ref *20*, and an electronic rapid method for determining contamination in coating raw materials (and by extension, preservation efficiacy) has recently been published [*21*]. Other methods are described in Ref *22*. Testing of algicides for tropical locations is described in Ref *23*.

CONSIDERATIONS FOR THE FUTURE DEVELOPMENT OF ANTIMICROBIAL AGENTS

While it is clear the development of new microbicides is both expensive and full of frustrations [*24*], some important results could ensue. The public is well aware of the potential harm to which people and the environment have recently been exposed and is pressuring the industry to move away from such products. However, few people will accept the purchase of a deteriorated material, and consumers expect the product to perform adequately once in use. Therefore, potentially less environmentally negative preservatives which are still effective have a place in the market and should be developed. Since the expense is exorbitant, this is going to be a slower process than one would like but should, nevertheless, proceed. The costs come from maintaining research and development departments, as well as application and development costs. The highest costs are incurred from required and necessary toxicology testing. With the goal of developing less toxic and more environmentally friendly biocides, these costs will surely increase with broader testing.

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30

Thickeners and Rheology Modifiers

by Gregory D. Shay[1]

LIST OF ABBREVIATIONS

AQ	Aqueous
ASE	Alkali-swellable and/or soluble emulsion
ATRM	Associative thickener and/or rheology modifier
BCARB	Butyl Carbitol®
BP	Biopolymer
CMC	Carboxymethyl cellulose
CTRM	Conventional thickener and/or rheology modifier
DS	Degree of substitution
DUEV	Dynamic uniaxial extensional viscosity
EHEC	Ethyl hydroxyethyl cellulose
HASE	Hydrophobe modified alkali-swellable/soluble emulsion
HBMC	Hydroxybutylmethyl cellulose
HEC	Hydroxyethyl cellulose
HEEASE	Hydrophobe modified ethoxylate ester alkali-swellable/soluble emulsion
HEMC	Hydroxyethylmethyl cellulose
HENN	Hydrophobe modified ethoxylate nonionic non-urethane
HEUR	Hydrophobe modified ethoxylate urethane
HEURASE	Hydrophobe modified ethoxylate urethane alkali-swellable/soluble emulsion
HMC	Hydrophobe modified cellulosic
HNS	Hydrophobe modified nonionic synthetic
HMEHEC	Hydrophobe modified ethyl hydroxyethyl cellulose
HMHEC	Hydrophobe modified hydroxyethyl cellulose
HPG	Hydroxypropyl guar
HPMC	Hydroxypropylmethyl cellulose
HSV	High-shear viscosity
ITRM	Inorganic thickener and/or rheology modifier
LIQ	Liquid
LSV	Low-shear viscosity
MC	Methyl cellulose
MS	Molar substitution
MSV	Medium-shear viscosity
NA	Data not available
ORG	Organo or organic
PAA	Polyacrylic acid
pEO	Polyethylene oxide
PG	Propylene glycol
PVC	Pigment volume concentration
RM	Rheology modifier
SOLV	Solvent
T	Thickener
TRM	Thickener and/or rheology modifier
VOC	Volatile organic components
XCPS	Xanthamonas campestris polysaccharide (Xanthan gum)

[1]Technology manager, Thickeners and Rheology Modifiers, Union Carbide Corp., UCAR Emulsion Systems, 410 Gregson Drive, Cary, NC 27511.

INTRODUCTION

DEMANDS ON THE APPLICATION and flow properties of coatings have increased substantially, and because thickeners and rheology modifiers (TRMs collectively) play a key role in performance, they are among the most important components in a coatings system. Although TRMs are used in minor amounts in most formulations and are generally considered additives, aqueous coatings usually contain at least one, often two, and sometimes several to obtain the desired balance of properties. Due to present-day environmental concerns and the use of TRMs predominantly in aqueous coatings, the focus of this chapter is on water-borne, and especially latex-based systems. TRMs also find utility in solvent-borne coatings where they function primarily as flow modifiers and thixotropes. These products are discussed in later sections of this chapter.

Thickeners

Thickeners, as traditionally defined, are components that substantially increase viscosity (resistance to flow) at relatively low concentrations. For coatings, thickeners are normally used to increase viscosity at moderate shear rates approximating those encountered during pouring, stirring, or mixing. The viscosity in this shear rate range is often referred to as the coating "consistency" or medium-shear viscosity (MSV). To be effective, a thickener should produce the desired consistency at a low-use level that is often expressed in units of lb thickener solids per 100 gal of liquid coating (g/L where metric units are used). For architectural coatings, the total amount of thickener typically used is less than about 15 lb/100 gal (~18 g/L) and can be as low as 3 lb/100 gal (~4 g/L) or less, depending on coating solids, pigment volume concentration (PVC), vehicle type, and other components present in the formulation. As discussed later, selection of components

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is particularly important with associative thickeners. The units of shear rate are reciprocal seconds (s^{-1}), and the shear rate range for measurement of consistency is about 10 to 1000 s^{-1} and more typically about 100 s^{-1}.

A change in a coating's consistency can be sensed subjectively. For example, the depth of fluid vortex in a container at a given mixing speed can be observed visually, or the increase in resistance to flow during hand stirring can be felt. The consistency of the coating can also be measured using an appropriate viscometer or rheometer that operates in the medium shear rate range (such as at 10 to 1000 s^{-1}). The high end of this range also correlates with "pumpability," which is critical in some automated manufacturing operations. Several popular instruments for measuring consistency are described later in this chapter under **Coating Consistency (Medium-Shear Viscosity).**

Rheology Modifiers

Presently, there is no universally accepted definition of the term "rheology modifier." In fact, the terms "thickener" and "rheology modifier" are often used interchangeably in commerce, especially for associative TRMs. All thickeners modify rheology to varying degrees when incorporated; consequently, all thickeners, technically, are also rheology modifiers. Some modify rheology in a positive way, and others modify rheology adversely depending on the desired effect. Although all thickeners can be considered rheology modifiers, not all rheology modifiers are considered thickeners, and herein lies a distinction. For purposes of classification, rheology modifiers are defined here as additives which influence viscosity at high and/or low shear rate (generally above 1000 s^{-1} or below 10 s^{-1}) but contribute little to consistency (that is, they change rheology but are inefficient thickeners). If a rheology modifier as defined was used as the sole thickener for consistency, typically more than about 15 lb/100 gal (~18 g/L) would be required, and 30 to 60 lb/100 gal (~35 to 75 g/L) would not be unusual. When used as primarily intended (as a rheology modifier with one or more other thickeners present), amounts much less than this normally suffice.

Like thickeners, rheology modifiers may also influence the elastic or elongational (extensional) properties of coatings, which can be measured on some relatively sophisticated rheometers. Frequently, a single thickener or combination of thickeners is effective in meeting all of the rheological requirements (low, medium, and high-shear) of a given coating formulation, and a rheology modifier is not needed in this situation. If the rheological requirements cannot be met with thickeners alone, a rheology modifier is often included to augment flow properties. A common example of this is the incorporation of a rheology modifier to raise the high-shear viscosity (HSV) of a coating. This increases viscosity on application which, in turn, provides increased film build (film thickness) for improved substrate protection or one-coat hiding.

In some situations, a rheology modifier is efficient enough to function as an effective thickener such as in the presence of a small-particle-size latex, water-insoluble coalescing aids, at high binder concentrations, or at high-volume solids. This effect, which will be discussed in detail later, especially applies to associative rheology modifiers where strong interactions occur between the TRM and other coating components.

INCORPORATION OF TRMs

Coating manufacturing operations generally consist of several stages of processing, and TRMs are important in each. Some common stages are the "premix" (ingredients added prior to pigments), "grind" (pigment added and reduced in size for optimum dispersion), and "letdown" (where polymer or latex is normally added). Some but usually not all of the thickener is added to the premix to increase viscosity in the grind for improved pigment dispersion (deagglomeration). Under laminar flow conditions, rate of shear during grinding is set by the tip speed of the impeller and the depth of the shear gradient. One theory suggests that increased viscosity allows better energy transfer by decreasing turbulence at the impeller, which, in turn, increases the shearing collisions that attrite the pigment agglomerates. However, too much thickener at this stage impedes mixing and actually slows down the grinding process. The remaining thickener is usually added to the letdown to provide proper suspension and product consistency. Finally, post-adjustments with additional thickener or rheology modifier may be required to bring the product "into specification" for application and appearance properties.

RHEOLOGY AND VISCOSITY

Because viscosity and rheology modification are the very essence of primary TRM function, a basic understanding of rheological concepts is helpful to fully appreciate differentiation in product performance. A thorough treatment of this subject is found elsewhere in this book. The following subsections provide a general overview of the two primary types of flow encountered during the preparation, storage, and application of coatings that are affected by the choice and amount of TRM present [*1–5*].

Shear Flow

Most low, medium, and high shear rate coating phenomena involve shear flow that is normally characterized in the laminar regime (where the shear field produces Reynold's Numbers below the critical characteristic for the fluid). Shear flow in the Turbulent regime (high Reynold's Numbers) is not normally characterized, since most parameterizing equations fail here. The vast majority of viscometers produce shear flow and measure the ratio of shear stress to shear rate (viscosity). With coatings, it is useful to determine viscosity at several shear rates to obtain a complete rheology profile which is normally represented in log-log form. These profiles are also conveniently divided into three shear rate regions—"at rest," "processing," and "application," which correspond to the low-shear, medium-shear, and high-shear regions, respectively, as depicted in Fig. 1. Optionally, the viscosity profile can be approximated by single-point measurements of low-shear viscosity (LSV), medium-shear viscosity (MSV), and high-shear viscosity (HSV). Some of the coating processes and

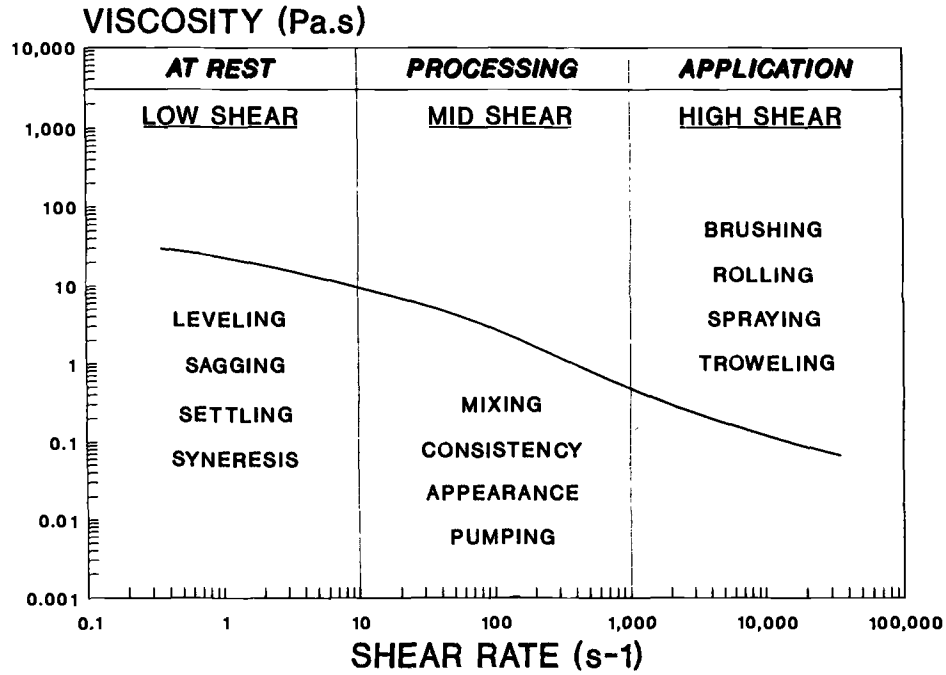

FIG. 1–A typical architectural coating viscosity profile, three important shear rate ranges, and the coating parameters affected and operating in each shear rate range.

properties affected in each region are also shown in Fig. 1 and are further discussed later in this chapter under **TRM FUNCTIONS.**

Time-dependent shear thinning (thixotropy) and zero-shear yield value are two other rheological coating properties that may be very important. For example, a thixotropic fluid with high yield value may exhibit good leveling if the time required to rebuild viscosity is long compared to the time needed for flowout. The viscoelastic properties of a coating may also be important. The elastic component of shear can be determined on some advanced cone-plate or parallel plate rheometers either by measuring the shear storage modulus (G') in oscillatory simple shear or by measuring normal forces (for example, first normal stress difference, N_1), which are perpendicular to the plane of shear.

Elongational Flow

In addition to the simple shear flow fields generated during the mixing and application of coatings, elongational (extensional) flows may also be induced during the application processes of spray, roll, or blade coating. The study of extensional flows and their importance in coatings has been examined [*6–11*]. During these application processes, the fluid is accelerated as it approaches the applicator orifice or nip, and the TRM polymer molecules become stretched and aligned. The viscosity related to the induced elongational flow is termed by Glass [*7*] as the "dynamic uniaxial extensional viscosity" (DUEV). One coating property that has shown some correlation with DUEV is roller spatter that can be rated using ASTM Test Method for Measurement of Paint Spatter Resistance to Roller Application (D 4707-87). Other properties that have shown some correlation with DUEV are ribbing, web formation, and misting in roll coatings, and the atomization process in spray coatings. Until recently, the measurement of DUEV on disperse phase coating systems was difficult; however, a commercial instrument is now available for measuring DUEV on undiluted coatings directly. As a class, associative thickeners tend to impart lower DUEV than conventional (nonassociative) thickeners, which improves some of the application properties described. Comparative representations of shear and elongational (extensional) flow are depicted in Fig. 2.

TRM CLASSIFICATION

Polymeric organic thickeners for aqueous media are often classified into two basic types: "conventional," which thicken predominately by hydrodynamic and flocculative mechanisms, and "associative," which thicken predominantly by associative mechanisms. Unfortunately, these are mechanistic

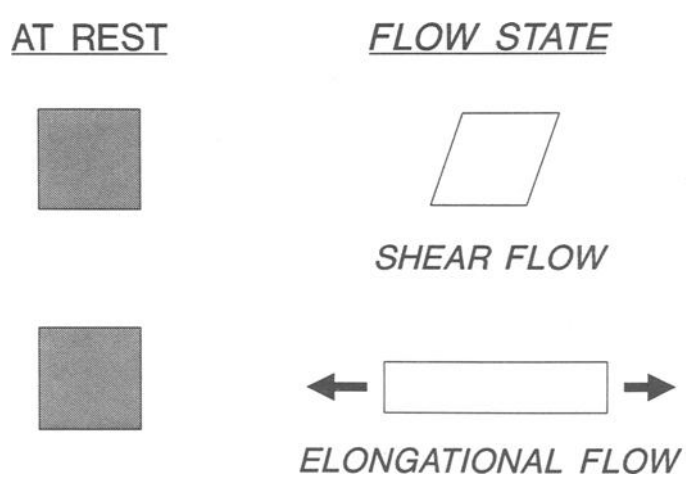

FIG. 2–Types of induced flow in coatings.

definitions that are subject to some variability and exception. A clear distinction, however, can be made for purposes of classification based on composition. Conventional (nonassociative) thickeners (CTRMs) are defined here as high-molecular-weight water-soluble polymers with relatively uniform hydrophilic backbones lacking hydrophobic groups. Lower-molecular weight species of similar chemical composition (analogs) are less efficient as thickeners but may serve as rheology modifiers. Associative thickeners (ATRMs), on the other hand, are defined here as water-soluble polymers of comparatively lower molecular weight which contain hydrophobic groups at the ends within or pendant to the hydrophilic backbones. The hydrophobes in these polymers are capable of nonspecific hydrophobic associations similar to those of conventional surfactants, and these associations are primarily responsible for generation of viscosity with these thickeners. Variation in chemical architecture, the number of hydrophobes present, and a further reduction in molecular weight can produce associative polymers which function primarily as rheology modifiers. It becomes readily apparent that, with proper hydrophobe modification, virtually any CTRM can be converted to an associative polymer, and this is what has been done in the design of several commercial ATRM products. The advantages and disadvantages of CTRMs and ATRMs have been reviewed in the literature [*12,13*] and will become more apparent in the following sections. A clearer distinction between these two major classes of TRMs will be apparent on examination of the thickening mechanisms involved. Although nearly all inorganic thickeners are conventional with respect to their thickening mechanisms, these TRMs will be treated separately later of this chapter under **INORGANIC THICKENERS FOR AQUEOUS AND SOLVENT-BORNE COATINGS.**

THICKENING MECHANISMS

The three primary thickening mechanisms for polymeric water-borne thickeners are "hydrodynamic," "flocculative," and "associative." Each of these mechanisms may be further divided into subclasses, if desired, which have their own individual rheological and coating characteristics. Consequently, it is important to consider these mechanisms when making TRM selection for increasing coating consistency, for rheology modification, or for other coating properties.

Thickening is often a complex process. For example, the flocculation mechanism is frequently a byproduct of hydrodynamic thickening but may also occur in associative systems that are improperly formulated or in those where a controlled degree of flocculation is desired. Some associative thickeners (for example, alkali-swellable types) are sufficiently high in molecular weight that an appreciable hydrodynamic component of thickening is also present. Depending on their chemical architecture, strength of the hydrophobic associations, and other formulation components present, some ATRMs actually function to varying degrees with several associative and nonassociative mechanisms at the same time. Outlined in Table 1 are some possible thickening mechanisms for conventional and associative thickeners.

TABLE 1—Thickening mechanisms for organic polymers in aqueous media.

I. *Hydrodynamic (CTRMs)*
(A) High MW soluble polymers
(B) Insoluble swellable polymers
II. *Associative (ATRMs)*
(A) Hydrophobe interactions
(B) Ion-dipole interactions
III. *Flocculative (CTRMs and ATRMs)*
(A) Depletion flocculation
(B) Bridging flocculation

NOTE: The flocculative mechanisms occur in disperse phase systems only and almost exclusively in the presence of CTRMs.

The Hydrodynamic Mechanism

Prior to the introduction of associative thickeners, nearly all organic thickeners used for aqueous coatings were water-soluble polymers of high molecular weight (MW) without hydrophobe modification, which is the collective criteria for their classification as conventional thickeners. The molecular weights of the conventional polymers that function as thickeners for water-borne coatings are generally greater than about 10^5 and can be as high as 10^6 or more. Polymers with stiff backbones (for example, cellulosics) at the lower end of the MW range are as effective in thickening in the high end of this range with flexible backbones (for example, polyethylene oxide). When conventional thickeners dissolve in water, the polymer chains occupy a large hydrodynamic volume in solution and immobilize large volumes of water within the coils of their backbones. This increases viscosity of the continuous water phase dramatically. For a given polymer type, higher molecular weight generates higher viscosity. In fact, the solution viscosity of conventional polymers in water or nonaqueous solvents is one of the common methods used for determination of molecular weight. As previously stated, sufficiently low-molecular-weight polymer analogs can function as true rheology modifiers since they do not contribute appreciably to consistency (MSV). However, these have been replaced to a large degree with associative rheology modifiers in many coatings applications.

Some conventional thickeners are lightly cross-linked to make them water-swellable rather than water-soluble. In aqueous media, these polymers swell significantly to produce viscosity by a hydrodynamic mechanism. When the polymers are made by emulsion polymerization, they may swell to many times their original particle size. Examples of conventional water-soluble or water-swellable thickeners used extensively in coatings are hydroxyethyl cellulose, hydroxypropyl methyl cellulose, and alkali-swellable/soluble copolymer emulsions (ASEs). These and some other CTRMs are discussed later in this chapter under **CONVENTIONAL TRMs (CTRMs).**

Flocculative Mechanisms

Because CTRMs take up so much volume in solution, they induce flocculation in coatings, forming latex-rich and thickener-rich domains by a mechanism commonly referred to as 'volume restriction," "volume exclusion," or "depletion" flocculation. This process is now recognized as the primary mode of thickening for conventional thickeners in disperse phase systems (such as, in coatings with pigment or latex particles

present) and has been examined in both experimental [*14–16*] and theoretical treatments [*17,18*] and more recently modeled by computer simulation [*19*]. The process begins when latex particles randomly approach each other, and when they are close enough (on the order of a random-coil thickener molecular diameter), thickener molecules are "excluded" from the interparticle region. The concentration gradient formed causes water to be osmotically "pumped" from between the particles driving them even closer together, which further concentrates the thickener molecules in the aqueous phase. Eventually, the latex particles touch, forming flocs which are readily observable on microscopic examination. This mechanism of thickening can adversely affect gloss and hiding and also may impart more shear thinning character and more viscoelasticity. Since these polymers are of high molecular weight, they also tend to impart high extensional viscosity to coatings. The combination of viscoelasticity and high extensional viscosity results in a tendency for spatter and increased rib pattern in roll coatings [*20*].

Another flocculative mechanism is "bridging" flocculation. In this mechanism, the polymer molecules partially adsorb onto latex or pigment particles. If the thickener molecules are sufficiently long and have a strong affinity for other particles, bridging can occur, forming flocs.

ASSOCIATIVE MECHANISMS

The primary thickening mechanism for ATRMs is via intermolecular hydrophobic association and association of the thickener hydrophobes with disperse phase (colloidal phase) hydrophobic components in the coating formulation [*21–24*]. When a water-soluble polymer contains both hydrophilic and hydrophobic moieties, the potential for associative interaction exists. Among the simplest associative structures are nonionic surfactants. These molecules have a hydrophilic polymer segment on one end (usually polyethylene oxide) and a hydrophobic group on the other (typically a long chain alkyl or alkyl aryl group). At a sufficiently high concentration known as the critical micelle concentration (CMC), these surfactants spontaneously form micelles in aqueous solution. At or above this concentration, the hydrophobes aggregate at the interior of the micelle, and the hydrophilic tails orient outward into the water phase. The key driving force for micellization is not the London Van der Waals attractive forces between hydrophobes, but rather the change in free energy on transfer of a hydrophobe in the aqueous phase to a more oil-like environment at the interior of the micelle.

If a hydrophobe is chemically attached to the other end of a nonionic surfactant, a simple associative thickener is formed. However, because the thickener has a hydrophobe at each end, micelle formation is not a favorable process and is not observed except for certain chemical architectures at extremely low concentrations. Instead, the associative molecules aggregate into a three-dimensional network structure that inhibits flow and raises the viscosity of the aqueous solution or coating. The driving force is similar to that for micelle formation. Although each associative polymer type has an optimum molecular weight, high molecular weight is not a requirement of associative thickeners, and most are significantly lower in molecular weight (typically <50 000) than conventional thickeners. To be viable in commerce, ATRMs usually have a few repeat hydrophile-hydrophobe units to increase molecular weight, thereby increasing the hydrodynamic contribution and also the association efficiency.

Another aspect of ATRMs is their interaction with colloidal components in a coating formulation. Whenever latex particles or hydrophobic pigments are present in a coating formulation, the hydrophobes on the associative thickeners can adsorb onto the hydrophobic particle surfaces, which results in a further increase in system viscosity and possible modification of rheology. The strength of the association is important, and depending on degree, a polymer can induce several types of equilibrium phase behavior including nonassociative volume restriction and associative bridging flocculation [*26*]. For comparison, diagrammatic representations of a conventional thickener and an associative thickener in the presence of latex particles are depicted in Figs. 3 and 4, respectively.

Although hydrophobe interaction is the predominate associative mechanism for ATRMs, some evidence suggests an additional associative mechanism which is hydrophilic rather than hydrophobic in nature. The proposed hydrophilic association is an ion-dipole interaction between surface carboxyl groups on the latex with the polyethylene oxide (pEO) segments in the associative thickeners [*25*]. When the ATRMs contain both carboxyl and ethoxylate functionality in the same molecule (for example, associative alkali-swellable/soluble polymers), both intermolecular and intramolecular ion-dipole associations are theoretically possible.

TRM FUNCTIONS

The primary function of TRMs are the control of viscosity and rheology throughout the applicable shear rate spectrum: consistency is measured and adjusted in the medium-shear-rate range, application properties in the high-shear-rate range, and film formation and container storage properties in the low-shear-rate range. The viscosities associated with these ranges may be referred to as the medium-shear viscos-

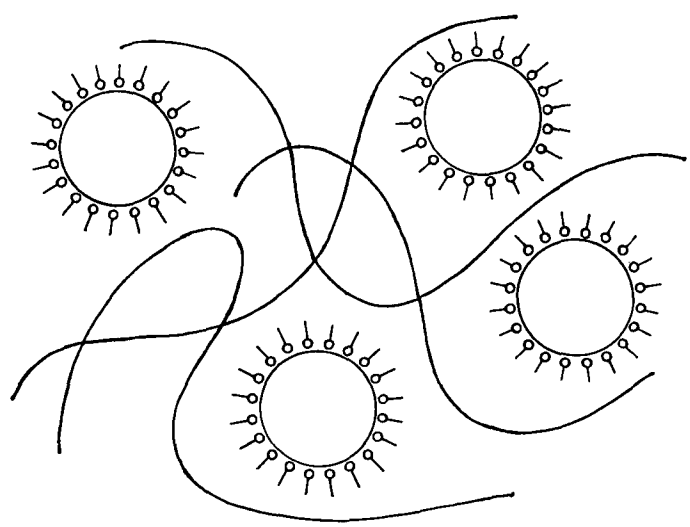

FIG. 3–Conventional (nonassociative) thickener molecules in the presence of aqueous latex particles.

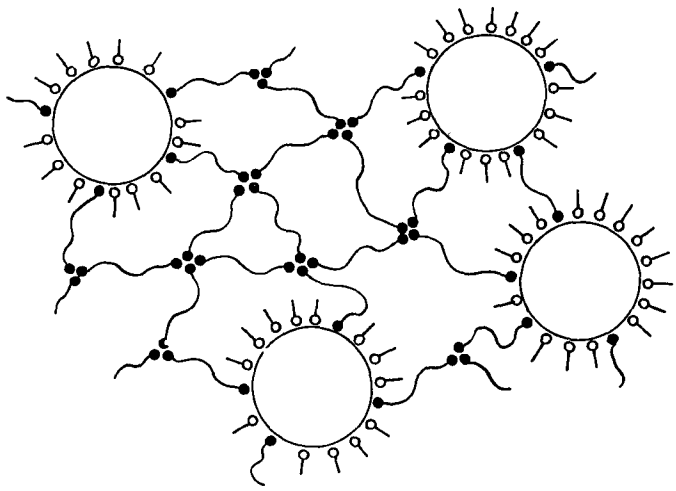

FIG. 4–Associative thickener molecules in the presence of aqueous latex particles.

ity (MSV), high-shear viscosity (HSV), and the low-shear viscosity (LSV), respectively. Several film properties are also affected and may be manipulated by the appropriate choice and amount of TRM in the coating [27]. Two examples of coatings improperly formulated with TRMs are represented in Fig. 5. A clear understanding of the rheology profiles depicted and their impact on application and film properties will become apparent in the following subsections.

Coating Consistency (Medium-Shear Viscosity)

Measurement of MSV in the previously defined medium-shear domain provides an indication of the consistency of a coating that relates to its appearance and feel on mixing. It is common practice for formulators to adjust coating viscosity in the medium-shear range by varying the amount of thickener added. The target viscosity is normally based on prior experience or on a previously established specification range for a particular type of coating. One popular rheometer used for measuring and facilitating consistency adjustment in architectural coatings is the Stormer® viscometer. Viscosity determination with this instrument is conducted in accordance with ASTM Test Method for Consistency of Paints using the Stormer Viscometer (D 562). This rheometer provides a paddle-type mixing action during measurement that is similar to stirring, and viscosity is expressed in Krebs Units (KU). Many coatings fall within the range of 60 to 120 KU, and a typical specification range for a semigloss architectural coating, for example, might be 90 to 95 KU.

The Brookfield® viscometer is another popular instrument for determination of consistency when operated at higher speeds (for example, 20 to 100 rpm). It is also useful at lower speeds (for example, 0.3 to 5 rpm) for determination of low-shear processes such as leveling [see later in this section under **Leveling, Sag, Syneresis, Settling (Low-Shear Viscosity)**]. Both of these measurements can be conducted in accordance with ASTM Test Method for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield) Viscometer (D 2196). Both the analog and digital Brookfield models provide viscosity in centipoise (mPa·s), and cylindrical spindles are commonly used for the measurement. Another Brookfield viscometer recently introduced has a paddle configuration similar to the Stormer viscometer. Readout on this model is in Krebs Units.

The Rotothinner® is another viscometer which can be used to determine consistency. It provides an even greater mixing action that is capable of stirring the entire container contents while the viscosity measurement is being made. While this instrument can be used for more conventional coatings, it is

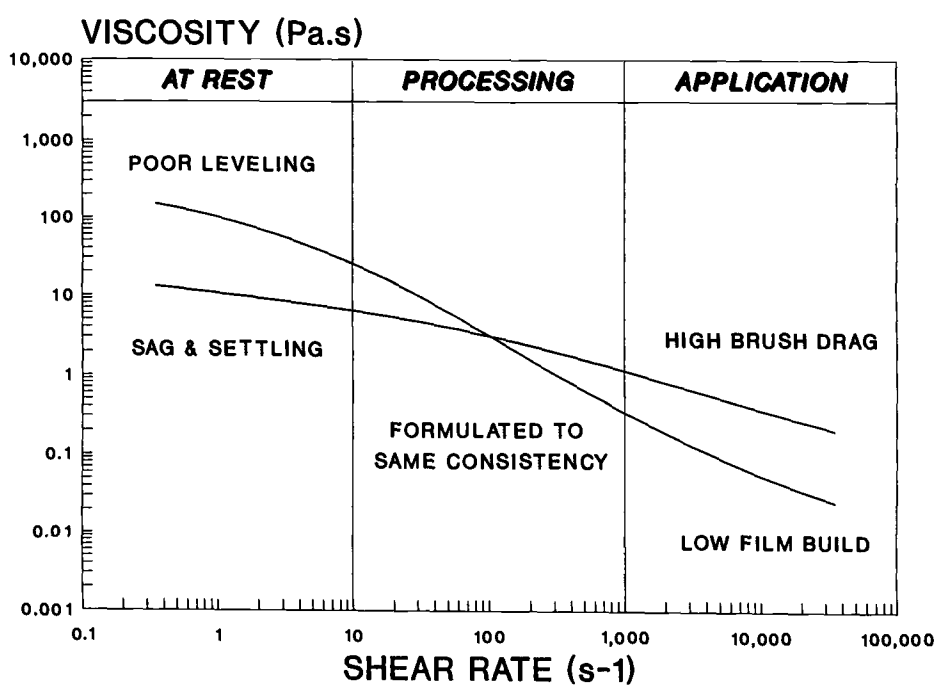

FIG. 5–Shear profile examples of inadequate TRM formulation for a premium architectural coating.

ideally suited for breaking down the structure of thixotropic fluids to obtain a sheared viscosity.

Application Properties (High-Shear Viscosity)

Most brush, spray, or blade coating operations are relatively high-shear processes. This is also true for roll coating applications when the circumferential velocity of the roll is significantly different than the linear velocity of the substrate. The shear on application for these operations is generally greater than about 10^3 s^{-1} and is typically about 10^4 s^{-1} for brushing and as high as 10^6 s^{-1} for some high-speed roll coating, blade coating, and spray operations. There are several high-performance rotational rheometers for measuring the HSV, and most use cone/plate or plate/plate geometry. One general purpose instrument that is popular for laboratory and quality control of HSV measurement is the ICI cone-plate viscometer by ASTM Test Method for High-Shear Viscosity Using the ICI Cone/Plate Viscometer (D 4287-88). This instrument has a fixed shear rate of 10^4 s^{-1}, and viscosity measured is a good predictor of film build when a coating is applied by brush or paint roller. The higher the ICI viscosity, the more resistance a brush or roller encounters on application, which results in a thicker applied film. HSVs at this shear rate are typically from about 0.5 to 2.5 P (50 to 250 mPa s) for architectural coatings. If the HSV is too high, the coating will require too much effort to apply, will have a low spread rate, and may sag. If the HSV is too low, a second coat may be required to hide the substrate. Subjective brush drag by actual application is often conducted in accordance with ASTM Test Method for Comparison of Brush Drag in Latex Paints (D 4958).

Conventional thickeners generally produce coatings with low HSV, while most associative thickeners and particularly associative rheology modifiers produce high HSV. Although not common, some associative thickeners produce low HSV that may be desirable depending on the application and film thickness desired. These thickeners tend to be very efficient in the medium-shear region, and the low HSV is primarily a consequence of less thickener being used. As a general rule for a given thickener type, the more thickener required to obtain desired consistency (MSV), the higher the HSV will be. Therefore, if an increase in HSV is desired, a less efficient thickener or a rheology modifier may be needed. As an option with associative thickeners, efficiency in the medium-shear region can be suppressed or enhanced by adjustment of other components in the coating formulation. By proper TRM selection or TRM blending, the desired HSV can be obtained without adversely affecting MSV or LSV.

Leveling, Sag, Syneresis, Settling (Low-Shear Viscosity)

After a coating has been made or applied, an appropriate LSV is needed to prevent container separation (pigment settling and syneresis) and to promote film formation (leveling and sag resistance). The applicable shear rates for LSV are generally less than about 10 s^{-1} and more practically in the range of 10^0 to 10^{-3} s^{-1}. The low-shear applied in these processes is primarily due to the effects of gravity for container separation and sagging and due to capillary pressure (generated by surface tension and surface curvature) for leveling. In architectural coatings, LSVs that are too high result in poor leveling, and brush or roller pattern is very apparent. The degree of leveling is often determined by simple inspection of brush marks or roller pattern after the applied film has dried. Optionally, a notched applicator on a horizontal surface may be used in accordance with ASTM Test Method for Leveling of Paints by Draw-Down Method (D 4062). In contrast, LSVs that are too low may allow sagging on vertical surfaces and in-can settling or syneresis. Sag ratings are often conducted in accordance with ASTM Test Methods for Sag Resistance of Paints using the Multinotch Applicator (D 4400).

A variety of viscometric techniques have shown some correlation with leveling. Among these is a stress-relaxation procedure [*28*]. In this method, the coating is first sheared at a moderately high rate to break down structure to simulate brushing or rolling. The shearing is then stopped, and the declining shear stress versus time is recorded. The area under the relaxation curve is then integrated to obtain a "leveling viscosity" (that is, the product of stress and time has the dimensions of viscosity).

A relatively simple one-point technique which generally provides good correlation with leveling is a viscosity measurement at low rpm (for example, 0.3 rpm on a Brookfield® viscometer). At the low shear rate produced at this speed, excellent leveling would be indicated for coatings with measured viscosities of less than about 250 P (25 Pa·s) as might be obtained with a high-performance associative thickener. Too much flow would be indicated below about 100 P (10 Pa·s), and sag would be predicted on vertical surfaces. By the same technique, poor leveling would be indicated at about 1000 P (100 Pa·s) as might be obtained from a moderately high MW conventional thickener, and little or no flow at 2000 to 3000 P (200 to 300 Pa·s) for some very high MW conventional or special associative thickeners. Another common method conducted on a Brookfield® viscometer is the measure of "pseudoplastic index." This is a two-point determination that is the ratio of two viscosities a decade apart in shear rate (for example, 0.3 rpm/3.0 rpm or most commonly 6 rpm/60 rpm). LSV is probed by extrapolation of viscosity to lower shear rates (lower rpm).

From the prior discussion, it follows that a high LSV is generally needed for suspension or low flow characteristics, while a low LSV or low yield value is needed to promote flow and leveling. Due to the associative mechanism, most, but not all, ATRMs provide low LSVs to impart excellent leveling characteristics. However, some alkali-swellable associative thickeners impart uncharacteristically high LSVs, and like very high MW CTRMs, these thickeners have utility as antisag or antisettling agents or for use in highly structured coatings (for example, texture paints). Although these thickeners are definitely associative by examination in aqueous solution, their unusual behavior in coatings may be due to their ability to impart a degree of flocculation. Although not as low as CTRMs, lower gloss levels observed for some of these thickeners support this conclusion. However, some of these thickeners actually produce very high gloss levels, which suggests that aqueous phase networking has a larger influence on rheology than expected and/or that the dispersant character for these thickeners is greater than expected. Conventional thickeners, on the other hand, nearly always are highly shear thinning with high LSVs due to the hydrodynamic and floc-

culative mechanisms operating. Consequently, the gloss and hiding imparted from these thickeners tends to be lower.

CONVENTIONAL TRMS (CTRMS)

In the broadest definition, conventional TRMs (CTRMs) are water-soluble polymers lacking hydrophobe modification (that is, they are nonassociative). The higher-molecular-weight polymers function primarily as thickeners, and the lower-molecular-weight polymers function as rheology modifiers. Their primary thickening mechanisms are hydrodynamic and flocculative. Although there are many different types of water-soluble polymers which could be used as TRMs in architectural and industrial coatings, only a few have been accepted for use due to factors relating to economics, bio-stability, water sensitivity, compatibility, production quality, ease of handling, or rheology. Those CTRMs which are currently used in coatings, some widely and others infrequently, are discussed in the subsections which follow. These fall into two major categories: polymers of biological origin (polysaccharides) and the synthetic alkali-swellable/soluble emulsions (ASEs). The polysaccharides may be further subdivided into modified cellulosics, guar derivatives, alginates, and "biopolymers." The bipolymers are of more recent origin and employ microorganisms as a means of production or modification. Table 2 lists conventional water-soluble polymers used as thickeners in both coatings and noncoatings applications. With respect to coatings only, nearly all have been tried, many were found unacceptable, some are currently used, some have been used in the past, and others may have future potential particularly if modified with hydrophobes for conversion to ATRMs. Table 3 details some important domestic (U.S.) suppliers of CTRMs and their respective products.

TABLE 2—Conventional water-soluble thickeners for coatings and noncoatings applications.

Cellulosic polysaccharides
Carboxymethyl cellulose (CMC)
Carboxymethyl hydroxyethyl cellulose
Ethyl hydroxyethyl cellulose (EHEC)[a]
Hydroxyethyl cellulose (HEC)[b]
Hydroxypropyl methyl cellulose (HPMC)[b]
Methyl cellulose
Biopolymer polysaccharides
Gellan gum
Rhamsan gum[a]
Whelan gum
Xanthan gum (XCPS)[a]
Other polysaccharides
Guar gum
Hydroxypropyl guar (HPG)[a]
Sodium alginate
Synthetic hydrocarbon polymers
Poly acrylamide and copolymers
Poly ethylene oxide (PEO)
Poly hydroxyethyl (meth)acrylate
Poly (meth)acrylic acid copolymers (ASE)[b]
Poly olefinic sulfonate copolymers
Poly vinyl alcohol (PVOH)
Poly vinyl pyrolidone[a]
Poly styrene/maleic anhydride (SMA)
Poly methylvinyl ether/maleic anhydride

NOTE: [a]These have some use in architectural coatings. [b]These have significant use in architectural coatings. All others have little or no current use in architectural coatings.

Cellulosics

Prior to the introduction of ATRMs, conventional cellulosics were by far the most commonly used TRMs in aqueous coatings. They still dominate, but their use is in decline today. The reduction has been somewhat offset with the introduction of associative cellulosics, which are discussed later in this chapter under **Hydrophobe Modified Cellulosics (HMCs).** Cellulose $(C_6H_{10}O_5)_n$ is a naturally occurring polysaccharide composed of repeating anhydroglucose units. Because of its relatively straight and stiff polymer chain and strong intermolecular and intramolecular hydrogen bonding, the polymer itself is highly crystalline and consequently insoluble in water. Nonetheless, with chemical modification, cellulose can be readily converted to amorphous water-soluble polymers. Hydroxyethyl cellulose (HEC), hydroxypropyl methyl cellulose (HPMC), carboxymethyl cellulose (CMC), and ethylhydroxyethyl cellulose (EHEC) are among those that have been used in aqueous coatings.

The reactions used to produce water-soluble cellulose polymers are relatively uncomplicated. They typically involve treatment of cellulose with alkali to swell the polymer, followed by the chemical addition of the appropriate substituent. Each of the commercial polymer types is available in a variety of grades that are differentiated by molecular weight, levels of substitution, uniformity of substitution, and treatment for ease of dispersion. As molecular weight increases for a given polymer type, the amount of thickener required for constant MSV decreases (thickening efficiency improves). At the same time, LSV increases and HSV decreases. The effect on film build is predictable (lower); however, some investigators have actually reported improved leveling with higher MW cellulosics. The modifications are defined in two ways: the degree of substitution (SD), which is the average number of hydroxyl groups which have been substituted per anhydroglucose unit, and the moles of substitution (MS), which is the average number of moles of substituents per anhydroglucose unit for those substituents which generate repeating units (such as ethylene oxide in HEC).

HEC

Of the cellulosics, hydroxyethyl cellulose unquestionably has been the most popular TRM used in coatings. HEC is a nonionic polysaccharide manufactured by reacting ethylene oxide with the reactive hydroxyls on the anhydroglucose units of cellulose. The ethylene oxide also reacts with previously substituted hydroxyls, resulting in short pEO side chains (usually two or three units in length). The ratio of molar substitution (MS) to degree of substitution defines the number of EO groups per side chain. The most popular products have MS values in the range of 1.5 to 3.0 and DS values of about 0.85 to 1.35. Optimizing reaction conditions results in a more uniform distribution of substitution to produce bio-resistant polymer grades.

Presently there are two major international producers of HEC, and the products are available in several regular and enzyme-resistant grades. Of these, the medium- and high-molecular-weight bio-resistant grades have been of greatest utility in coatings as thickeners. Low-molecular-weight grades are used as secondary TRMs to modify rheology (improve flow or film build). Some grades also have surface treat-

TABLE 3—Conventional TRMs (CTRMs)—U.S. suppliers and trade names for aqueous architectural and industrial coatings.

Company Code	TRM Trade Name	TRM Code	TRM Class	Solids, %	Typical Viscosity, mPa·s	Co-solvent	Water in Volatiles, %
1	Alcogum®	L-11	ASE	28.0	14	None	100
1	Alcogum®	L-12	ASE	29.0	50	None	100
1	Alcogum®	L-15	ASE	30.0	50	None	100
1	Alcogum®	L-27	ASE	20.0	50	None	100
1	Alcogum®	L-31	ASE	40.0	20	None	100
1	Alcogum®	L-36	ASE	20.0	50	None	100
1	Alcogum®	L-45	ASE	40.0	20	None	100
1	Alcogum®	L-52	ASE	30.0	50	None	100
2	Aqualon®	7 Series	CMC	100.0	Solid	None	...
2	Aqualon®	9 Series	CMC	100.0	Solid	None	...
2	Natrosol®	250R Series	HEC	95.0	Solid	None	...
2	Natrosol®	250B Series	HEC	95.0	Solid	None	...
2	Natrosol®	FPS® HB	HEC	20.0	7000	None	100
2	Natrosol®	FPS® MB	HEC	20.0	7000	None	100
2	Natrosol®	FPS® G	HEC	25.0	7000	None	100
6	Methocel®	J Series	HPMC	100.0	Solid	None	...
6	Methocel®	K Series	HPMC	100.0	Solid	None	...
10	Carbopol®	600 Series	PAA	100.0	Solid	None	...
10	Carbopol®	900 Series	PAA	100.0	Solid	None	...
13	Aqua Thix®	...	HPG	100.0	Solid	None	...
14	Rhamsan	K7C233	BP	100.0	Solid	None	...
14	Welan	K1A96	BP	100.0	Solid	None	...
14	Kelzan®	Xanthan	XCPS	100.0	Solid	None	...
14	Kelzan® S	Xanthan	XCPS	100.0	Solid	None	...
14	Kelgin®	F, MV, HV	Algin	100.0	Solid	None	...
15	Flocon®	4800	XCPS	4.0	4000	None	100
15	Flocon®	4800C	XCPS	13.5	13000	None	100
18	Colloid®	1560	ASE	28.0	5	None	100
19	Acrysol®	ASE-60	ASE	28.0	4	None	100
19	Acrysol®	ASE-75	ASE	40.0	20	None	100
19	Acrysol®	ASE-95	ASE	18.0	50	None	100
19	Acrysol®	ASE-108	ASE	20.0	200	None	100
19	Acrysol®	G-110	ASE-NH4	22.0	130	None	100
19	Acrysol®	GS	ASE-Na	12.5	15000	None	100
19	Acrysol®	HV-1	ASE-Na	10.0	17500	None	100
23	Cellosoze®	QP Series	HEC	100.0	Solid	None	...
23	Cellosoze®	ER Series	HEC	100.0	Solid	None	...
25	Rhodopol®	23	XCPS	87.0	Solid	None	...
25	Rhodopol®	50MD	XCPS	87.0	Solid	None	...

ments to slow down the rate of hydration to minimizes lumping. Until recently, HEC was only available in solid form. Moderately viscous "fluidized dispersions" are now available which improve handling and increase the rate of incorporation. To minimize the dispersion viscosity of the supplied product, proprietary salts are incorporated. Various test methods for HEC are found in ASTM Test Methods for Hydroxyethylcellulose (D 2364).

HPMC

Hydroxypropyl methyl cellulose, a derivative of water-soluble methyl cellulose (MC), is another nonionic polysaccharide which has wide acceptance in coatings. Two other lesser known water-soluble analog derivatives of MC are hydroxyethyl methyl cellulose (HEMC) and hydroxybutyl methyl cellulose (HBMC). Grades of HPMC vary in molecular weight [*29*], the ratio of methyl to hydroxypropyl substitution on the cellulose backbone, and the degree of substitution. Commercial grades of HPMC have average DS for the methyl groups in the range of 0.9 to 1.8 and MS for hydroxypropyl groups in the range of 0.1 to 1.0. Variations in these parameters affect solubility, thermal properties, and resistance to enzymes. Both MC and HPMC exhibit lower critical solution temperatures (i.e., they possess the somewhat unusual property of being soluble in cold water and insoluble in hot water). Solutions of these polymers form gel structures on heating. With modifications in processing, DS, MS, the gel temperature, and gel texture are altered. Because of its structure, HPMC is also inherently more resistant to bio-organisms compared to some other polysaccharides. Various test methods for the

characterization of HPMC may be found in ASTM Test Methods for Hydroxypropyl Methylcellulose (D 2363).

EHEC

Ethyl hydroxyethyl cellulose is another water-soluble polymer with utility in water-borne paints with many properties similar to HPMC. The principal commercial product line consists of two series where the degree of molar substitution for the hydroxyethyl group is 0.8 and 2.1, respectively, and the ethyl group is the same for all grades with DS of approximately 0.8. All grades are also available with surface treatment for fast dispersion and adjustable dissolution rate. Like HPMC, EHEC is soluble in cold water and insoluble in hot water. Increasing hydroxyethyl substitution increases water solubility, improves salt tolerance, and decreases the tendency for gellation on heating.

CMC

Sodium carboxymethyl cellulose (CMC) is an anionic water-soluble polymer which has been of limited use in coatings because the modification constituent (sodium carboxylate) leaves the dried films more water-sensitive than most nonionic polysaccharides. CMC is prepared by reaction of cellulose with monochloroacetic acid after treatment with alkali. Commercial grades have DS for carboxylate substitution ranging from 0.4 to 1.4, and the most popular products are MS 0.7 to 0.8. As with most other conventional polysaccharides, the viscosity is primarily controlled by varying the molecular weight of the cellulosic chain. Some technical grades of CMC contain by-product salts (primarily sodium chloride and sodium glycolate) that further limits their use in coatings applications (for example, to dry-mix paints where the CMC functions to control viscosity and wet edge). A purified grade referred to as cellulose gum is preferred for use in latex paints. Various procedures for characterization of CMC may be found in ASTM Test Methods for Sodium Carboxymethylcellulose (D 1439).

Hydroxypropyl Guar (HPG)

Of the noncellulosic polysaccharides available for use in coatings, only hydroxypropyl guar (HPG) has found significant application. HPG is a chemical modification of guar gum which is a high-molecular-weight galactomannan obtained from the seeds of two leguminous plants (*Cyamopsis tetragonalobus* and *psoraloides*). Like the biopolymers described below, this polymer produces coatings which are more shear thinning (more pseudoplastic) than the cellulosic products. Hence, compared to cellulosics, HPG tends to have better suspension and antisag characteristics but produces more roll spatter and is less bio-resistant. Another limitation for HPG is that it is available in only one grade. Compared with its parent (guar gum), solutions of HPG are more bio-resistant, less electrolyte sensitive, and have improved solubility and clarity. Utility of HPG is primarily as a secondary thickener or for use in flat, texture, and dripless paints.

Biopolymers

The use of biopolymers in paints and coatings has also been limited; nonetheless, at least two products are being used as either primary or secondary thickeners to provide suspension characteristics. Commercial biopolymers are polysaccharides; however, they differ from the cellulosic and guar products described above in that they are enzymatically produced rather than being made by chemical modification. The biopolymer synthesis is typically conducted in a fermentation broth with bacterium or yeast. Seemingly common to the biopolymers is their ability to suspend or gel, their salt tolerance, and their stable viscosity over a wide temperature range. As with HPG, a limitation is that there are only one or two grades available from each supplier. Among the commercial biopolymer products which are available are Xanthan gum, Rhamsan gum, Welan gum, and Gellan gum.

Xanthan Gum

Perhaps the most well known and commercially important biopolymer is Xanthomonas campestris polysaccharide (XCPS), better known as Xanthan gum. This polymer was initially "cultured" in USDA laboratories using fermentation technology with the bacterium *Xanthomonas campestris* [*30*]. Xanthan gum is a high-molecular-weight (approximately 2×10^6), branched polysaccharide which is characterized as having high yield values and a high degree of pseudoplasticity (high LSV and low HSV). Total and immediate recovery of viscosity after shearing is also characteristic. Other features are its relative insensitivity to pH, temperature, and the presence of most salts. Applications for Xanthan are similar to those for HPG with somewhat better efficiency and even more shear thinning rheology (higher LSV). Xanthan gum is normally sold as a solid; however, liquid versions of this polymer (Xanthan broths) are now available that are easier to handle—supplied at relatively low concentrations (3 and 15%) with viscosities of about 4000 and 14 000 mPa·s, respectively. The side-chain functionality of the fluid polymer is significantly different (much higher in pyruvate content) from conventional solid Xanthan, but the rheology is still very shear thinning. The active biopolymer in these products is also claimed to be a more effective viscosifier than solid Xanthan.

Rhamsan Gum

Rhamsan gum is another biopolymer that has some application in coatings. One of the more outstanding characteristics of this polymer is its exceptional suspending power (produces very high LSV in coatings). In approximate order of decreasing suspending ability are Rhamsan gum > Xanthan gum > HP guar > CMC > HEC < CMC. Rhamsan gum also reportedly has good salt tolerance and improved stability to high-shear mixing.

Alkali-Swellable/Soluble Emulsions (ASEs)

ASEs are among the few conventional synthetic hydrocarbon thickeners to be used in substantial amounts in coatings. Conventional ASEs are carboxyl functional copolymers produced by the free-radical emulsion polymerization of ethylenically unsaturated monomers [*31*]. They are low-viscosity water-insoluble latexes at low pH as supplied, but exhibit thickening on dissolution or swelling of the latex particles when the pH is raised (generally above pH 5.5). Copolymers of methacrylic acid and ethyl acrylate are most common and

may contain a small amount (generally less than 1%) of a polyfunctional monomer to lightly cross-link the polymer to enhance swellability. Since most coating formulations are finished on the basic side, the ASE polymers are fully neutralized in most applications. They achieve their maximum viscosities above about pH 7, and, ideally, viscosity generated should be constant between about pH 7 to 10 so that slight changes in pH have little effect on coating consistency. Although ASEs impart rheology similar to other conventional thickeners, their primary advantages compared to the polysaccharides are in ease of handling and bio-stability. ASEs may be more water sensitive than most nonionic polysaccharides; however, unlike CMC, which is supplied as a sodium salt, neutralization of ASEs is normally with ammonia or volatile aminoalcohols which leave the film on drying. Hydrophobe modification of conventional ASEs to produce associative TRMs (HASEs) has greatly increased the popularity of the emulsion thickeners. These are discussed later in this chapter under **Hydrophobe Modified ASEs (HASE).**

ASSOCIATIVE TRMS (ATRMS)

Because of the increasing importance of rheology modification in coatings, the use of ATRMs continues to grow with many product offerings now available. Presently, three broad classes of commercial ATRMs represent many older and newer products. They are hydrophobe-modified nonionic synthetics (HNS), hydrophobe-modified cellulosics (HMC), and hydrophobe-modified alkali-swellable/soluble emulsions (HASE). Contained within the major classes are important subclasses all of which are discussed in detail below. Table 4 summarizes the commercial product classification scheme for ATRMs, principal subclass examples, and the designated acronyms. Those acronyms that are prominent in the literature as well as those which are newly assigned are indicated. Table 5 lists some important U.S. suppliers of ATRMs, their representative products, and the product's classification.

Coating components and coating formulation variables are known to affect the rheological performance of associative thickeners [*32,33*]. Some specific parameters which have been examined are volume solids [*34*], type of latex binder [*35,36*] latex binder particle size [*14,15*], particle surface acid groups [*25,37*], surfactants and cosolvents [*38*], coalescing aids [*39*], and some clay pigments [*40,41*]. The steady shear and linear viscoelastic properties of associative thickener solutions have also been characterized [*42*].

TABLE 4—Classification of associative thickener/rheology modifiers (ATRMs).

HNS—*Hydrophobe modified nonionic synthetic*
Subclass Example:
HEUR—Hydrophobe modified ethoxylate urethane
HENN—Hydrophobe modified nonionic non-urethane
HMC—*Hydrophobe modified cellulosic*
Subclass Example:
HMHEC—Hydrophobe modified hydroxyethyl cellulose
HMEHEC—Hydrophobe modified ethyl hydroxyethyl cellulose
HASE—*Hydrophobe modified alkali-swellable/soluble emulsion*
Subclass Example:
HEEASE—Hydrophobe modified ethoxylate ester alkali-swellable/soluble emulsion
HEURASE—Hydrophobe modified ethoxylate urethane alkali-swellable/soluble emulsion

NOTE: HNS, HENN, and HEEASE are new acronyms for which there were none previously. All others are those of general acceptance in ACS and other technical publications.

Hydrophobe Modified Nonionic Synthetics (HNS)

The HNS ATRMs are nonionic condensation polymers of synthetic origin. Common to these polymers are hydrophilic pEO segments which alternate with hydrophobic groups. The polymers tend to be much lower in molecular weight than conventional thickeners, and the repeat units (pEO segment plus hydrophobe) are generally less than about 20. Main chain ends and any side chains are typically terminated with hydrophobic groups. The two principal subclasses are hydrophobe-modified ethoxylate urethanes (HEUR) and hydrophobe-modified nonionic nonurethanes (HENNs). Differentiation in this classification scheme is simply the presence or lack of urethane functionality.

HEUR (Subclass of HNS)

The HEUR polymers are the major subclass of the nonionic synthetics (HNS). They are among the most popular ATRM products, and presently there are several domestic and international suppliers. Common to all HEUR polymers are the presence of three chemical components (terminal hydrophobes at the ends of side or main chains, internal hydrophilic pEO segments, and urethane linkages). The HEUR polymers are generally considered to be among the best of the associative products with respect to rheology modification. Being low in molecular weight and highly associative, they tend to provide the most Newtonian rheology (low LSVs and high HSVs) for superior flow/leveling and film build and also impart low extensional viscosity and low viscoelasticity for superior spatter resistance.

Nearly all HEUR polymers are supplied as moderately viscous solutions in a combination of water and cosolvent (for example, Butyl Carbitol® or propylene glycol). The cosolvent is present to suppress viscosity for ease of handling. Since HEURs are nonionic, they should have inherently low water sensitivity. However, they are generally less efficient than cellulosics or ASEs, and they are also much lower in molecular weight, which may limit their use in some exterior applications. Because the HEUR products have very low LSVs for superior flow, they may permit sagging, syneresis, or pigment settling, particularly when used as the sole thickener. They are also very sensitive to other coating components, and proper formulation balance is necessary for optimum performance. The HEUR products have been the subject of numerous technical investigations [*43–45*].

HENN (Subclass of HNS)

Synthetic nonionic associative thickeners lacking urethane functionality are the latest entry into the ATRM arena. At this writing, there is one commercial offering and two developmental products. Being synthetic, nonionic, and containing terminal hydrophobes, the chemical makeup of HENN polymers is generally similar to HEUR with the exceptions that the polyether segments may not be limited to ethylene oxide alone (that is, EO-PO blocks may be present), the molecular weights may be lower than some HEURs, and the products lack urethane linking groups (may contain ether, amide, or

TABLE 5—Associative TRMs (ATRMs)—U.S. suppliers and trade names for aqueous architectural and industrial coatings.

Company Code	TRM Trade Name	TRM Code	TRM Class	TRM Subclass	TRM Type	Total Solids, %	Typical Viscosity, mPa·s	Co-solvent	Water, %
1	Alcogum®	PT-33	HASE	HEEASE	T	30.0	20	None	100
1	Alcogum®	SL-70	HASE	HEEASE	T	30.0	20	None	100
1	Alcogum®	SL-76	HASE	HEEASE	T	30.0	20	None	100
1	Alcogum®	SL-98	HASE	HEEASE	T	30.0	20	None	100
2	Natrosol®	Plus 330	HMC	HMHEC	T	95.0	Solid	None	100
2	Natrosol®	Plus 430	HMC	HMHEC	T	95.0	Solid	None	100
2	Natrosol®	FPS® Plus 330	HMC	HMHEC	T	25.0	7000	None	100
2	Natrosol®	FPS® Plus 330	HMC	HMHEC	T	25.0	7000	None	100
11	DSX	1514	HNS	HEUR	T	40.0	3000	NA	NA
11	DSX	1550	HNS	HEUR	T	40.0	1500	NA	NA
17	Rheolate®	1	HASE	HEEASE	T	30.0	30	None	100
17	Rheolate®	101	HASE	HEEASE	T	100.0	Solid	None	100
17	Rheolate®	300	HNS	HENN	T	32.0	2400	BCARB	82
19	Acrysol®	RM-3	HASE	HEEASE	RM	30.0	50	None	100
19	Acrysol®	RM-4	HASE	HEEASE	RM	30.0	50	None	100
19	Acrysol®	RM-5	HASE	HEEASE	RM	30.0	100	None	100
19	Acrysol®	RM-825	HNS	HEUR	T	25.0	2500	BCARB	75
19	Acrysol®	RM-1020	HNS	HEUR	RM	20.0	2500	BCARB	88
19	Acrysol®	RM-2020	HNS	HEUR	RM	20.0	3000	None	100
19	Acrysol®	QR-708	HNS	HEUR	T	35.0	3500	PG	40
19	Acrysol®	TT-615	HASE	HEEASE	T	30.0	110	None	100
19	Acrysol®	TT-935	HASE	HEEASE	T	32.0	30	None	100
19	Acrysol®	TT-950	HASE	HEEASE	T	30.0	40	None	100
19	Acrysol®	SCT-200	HNS	HEUR	T	20.0	4800	BCARB	80
19	Acrysol®	SCT-215	HNS	HEUR	T	15.0	10000	BCARB	80
19	Acrysol®	SCT-270	HNS	HEUR	T	20.0	10000	BCARB	80
19	Acrysol®	SCT-275	HNS	HEUR	T	17.5	3000	BCARB	75
22	Ucar® Polyphobe®	101	HASE	HEURASE	T	25.0	50	None	100
22	Ucar® Polyphobe®	102	HASE	HEURASE	T	25.0	50	None	100
22	Ucar® Polyphobe®	103	HASE	HEURASE	T	25.0	50	None	100
22	Ucar® Polyphobe®	104	HASE	HEURASE	T	25.0	50	None	100
22	Ucar® Polyphobe®	107	HASE	HEURASE	T	25.0	50	None	100
22	Ucar® Polyphobe®	106HE	HASE	HEURASE	T	25.0	50	None	100
22	Ucar® Polyphobe®	111	HASE	HEURASE	T	25.0	50	None	100
23	Ucar® Polyphobe®	9820	HASE	HEURASE	T	25.0	50	None	100
23	Ucar® Polyphobe®	9823	HASE	HEURASE	RM	25.0	50	None	100
23	Cellosize® Spatter Guard®	100	HMC	HMHEC	T	95.0	Solid	None	100

some other linkage). Like the HEUR polymers, HENN thickeners contain cosolvent and are supplied as moderately viscous aqueous solutions. Little information is currently available; however, based on advertising claims for chemical composition and performance, the rheological characteristics of these products are expected to be similar to HEUR ATRMs. The chemical composition and physical form would also suggest that the handling and performance limitations are similar to those of HEURs. Improved color acceptance, color stability, and block resistance are claimed for the commercial product, and improved shear stability due to lower molecular weight is claimed for the developmental products but at the expense of thickening efficiency [*46*].

Hydrophobe Modified ASEs (HASE)

The HASE polymers were among the first ATRMs to be developed, and their commercial significance dates back to the late 1960s [*47–49*]. The popularity of these products continues due to their relatively good economics, bio-stability, rapid viscosity equilibration, lack of cosolvents (0 or low VOC), and low-viscosity liquid form as supplied. Like ASEs, the HASE products are synthetic addition polymers produced by emulsion polymerization of carboxyl functional monomers. Consequently, they are of relatively high molecular weight (higher than HNS but lower than conventional thickeners) and thicken by a hydrodynamic mechanism in addition to the associative mechanism. The predominate mechanism operating depends on several factors including the molecular weight and the amount and type of associative functionality.

Typically, HASE products are terpolymers of ethyl acrylate, methacrylic acid or itaconic acid, and an associative macromononer. The macromonomer usually contains pEO units (typically 10 to 100 mol ethylene oxide) terminated with a hydrophobe (typically alkyl or alkylaryl). The associative side chain linkage to the main chain backbone is predominately either ester (HEEASE) or urethane (HEURASE) per the classification scheme of Table 4. The patent literature does describe other linkages, and although some have been used in

the past, they are not commercial today (for example, products with ether linkages were marketed in the 1960s but were later discontinued). Like ASEs, the HASE polymers may also be cross-linked to varying degrees with small amounts (typically less than 1%) of a polyfunctional monomer to increase swellability. Although HASE polymers are anionic and, therefore, predicted to be more water sensitive than nonionic ATRMs, many HASE products are more efficient (less thickener is required for consistency), which minimizes the effect of the anionic character. Additionally, performance of HASEs in exterior coatings can be improved with ZnO or zinc complexes which cross-link the carboxyl functionality present [*50,51*], which is lacking in the HNS polymers. Being polyanionic, the HASE polymers also have dispersant character that contributes to hiding and gloss. The carboxyl groups in HASE polymers can also covalently cross-link with melamine, urea, and epoxy resins in thermoset coatings, and being acidic, they catalyze the cross-linking process.

HEEASE (Subclass of HASE)

The HEEASE polymers are one of two major HASE subclasses. Prior to the recent introduction of HASEs containing urethane linkages, the many commercial HEEASE polymers were the only representatives of the HASE class. Consequently, HASE usually implied HEEASE in the literature. Since there are now several commercial urethane functional HASE polymers, subclassification was needed, and like the HEUR and HENN polymers, differentiation here relates to the presence or lack of urethane linking functionality. The associative side chains of HEEASE polymers contain ester linkages, and like most other ATRMs, some HEEASE polymers are true rheology modifiers [*48*], and others are primarily thickeners providing relatively good associative rheology [*37,52*]. Because of the dual thickening mechanisms, the molecular weight and type and amount of associative functionality are among the processing variables that can be altered to effect change in performance. With respect to rheology, the HEEASE thickener performance is generally similar to the associative cellulosics.

HEURASE (Subclass of HASE)

The HEURASE ATRMs are a relatively new technology, combining much of the chemical architecture and advantage features of the anionic ASE and nonionic HEUR thickeners [*53–55*]. Like conventional ASEs, HEURASE polymers are prepared by emulsion polymerization and supplied as low-viscosity, low-pH latexes. However, the associative side chains in HEURASE contain the same three functional components found in HEUR thickeners (terminal hydrophobes, pEO segments, and urethane linkages). Because of this and the relatively high level of associative monomer present in these terpolymers, rheology modification approaching that of the premium HEUR thickeners is claimed without many of the HEUR and HENN limitations. Although most HEURASE thickeners provide the expected Newtonian rheology, some atypically impart suspension characteristics (high LSV) for use in antisag, antisettling, or texture paint applications. The extensional viscosity imparted by HEURASE products is low and comparable to some HEUR thickeners [*54*].

Hydrophobe Modified Cellulosics (HMCs)

Like the HNS polymers, hydrophobe-modified cellulosics are condensation polymers but of biological origin. These polymers are prepared by modifying standard or special grades of conventional cellulosics with hydrophobes. And, like the other ATRMs described above, the hydrophobes are typically alkyl or alkylaryl, but the pEO chains are comparatively very short. Presently there are two commercial subclasses of HMCs: hydrophobe-modified hydroxyethyl cellulose (HMHEC) and hydrophobe-modified ethyl hydroxyethyl cellulose (HMEHEC). These HMCs are presently all nonionic; however, the potential exists for future products which may be either nonionic [for example, hydrophobe-modified hydroxypropyl methyl cellulose (HMHPMC) and the like] or anionic [for example, hydrophobe-modified carboxymethyl cellulose (HMCMC) and the like].

HMHEC (Subclass of HMC)

The first commercial associative cellulosic thickener on the market in the late 1980s was hydrophobe-modified hydroxyethyl cellulose (HMHEC). This product has overcome many of the limitations of conventional HEC including improved film build, improved leveling, and better spatter resistance [*56*]. The associative behavior (adsorption onto latex and pigment particles) and the rheology of this polymer have been characterized [*57*] along with various solution properties [*58*]. The improvement in rheology (more Newtonian for better leveling and increased film build) over HEC is generally similar to the HEEASE thickeners, but since HMHEC is nonionic, the water sensitivity of coatings made with it tends to be better. The methods of preparation and solution properties of HMHEC have also been described [*59,60*]. HMHEC is prepared by attaching hydrophobes to conventional HEC via the hydroxyl groups along the polymer backbone. The degree of substitution and molecular weight grade of HEC chosen for this modification are important. Presently, there are two domestic commercial suppliers of HMHEC. One employs alkylaryl hydrophobe modification and the other aliphatic hydrophobe modification. Unlike other classes of ATRMs, the ethoxylate content between hydrophobe and HEC backbone is small (generally one to a few units). Because HMHEC is a solid, the handling limitations are similar to those of HEC and other solid thickeners. To party overcome this limitation, developmental fluidized aqueous dispersions of HMHEC are now available which are analogous to those now commercial for conventional HEC. The viscosity of the fluidized products as supplied is still moderately high and similar to that of the HEUR and HENN products.

HMEHEC (Subclass of HMC)

Associative EHEC polymers were introduced in 1992 and are the most recent HMC products. Being relatively new, little is known about them; however, their chemical construction and performance is expected to be similar to HMHEC. At this writing, there is currently only one nondomestic supplier of these products.

INORGANIC THICKENERS FOR AQUEOUS AND SOLVENT-BORNE COATINGS

Most inorganic thickeners and rheology modifiers (ITRMs) are supplied as powders. When they are properly dispersed into a coating, they usually function as suspending or gelling agents and some may have secondary utility as extender pigments. Rheologically, ITRMs tend to have high yield values and are characterized as "thixotropes." The viscosity of the coating decreases with time under constant shear as its gel structure is broken down. When the shear is removed, the coating gradually recovers to its original viscosity. The rate of recovery can be very rapid (complete within seconds) or can take several minutes or even hours depending on the degree of thixotropy and prior shear history. Certain grades or mineral types of ITRMs are useful for thickening aqueous systems and others for solvent-borne coatings. Utility in one media or the other is mostly a function of the thickener's particle surface, which is often modified with organic treatments to render it hydrophilic (usually for water-borne coatings) or hydrophobic (usually for solvent-borne coatings). ITRMs are also sometimes added to aqueous formulations as secondary thickeners to impart some degree of antisag, antisettling, or antisyneresis to coatings containing primary conventional or associative thickeners. The most common types of modified and unmodified ITRMs are attapulgite clays, bentonite clays, organoclays, and treated and untreated synthetic silicas [*61*]. Table 6 details some important domestic (U.S.) suppliers of modified and unmodified ITRMs for aqueous and solvent-borne coatings systems.

Attapulgite Clays

The attapulgite clays are the most commonly used ITRMs in latex paints because they are economical and also function as extender pigments. The principal mineral in attapulgite

TABLE 6—Inorganic TRMs (ITRMs)—U.S. suppliers and trade names for aqueous and solvent-borne architectural & industrial coatings.

Company	TRM Trade Name	TRM Code	TRM Class	System Use	Form, mPa·s	Total Solids, %
3	Cab-o-sil®	L, M, H Series	Fumed Silica	AQ/SOLV	Solid	100
3	Cab-o-sil®	TS Series	Treated Fumed Silica	AQ/SOLV	Solid	100
3	Cab-o-sperse®	A Series	Fumed Silica	AQ	LIQ	12
4	Neosyl®	TS	Precipitated Silica	AQ/SOLV	Solid	100
4	Gasil	DP	Precipitated Silica	AQ/SOLV	Solid	100
5	Aerosil®	130–380 Series	Fumed Silica	AQ	Solid	100
5	Aerosil®	R972, R974	Fumed Silica	SOLV	Solid	100
7	Korthix®	Regular	Refined Bentonite	AQ	Solid	100
7	Korthix®	H	Refined Modified Bentonite	AQ	Solid	100
8	Attagel®	40 & 50	Attapulgite Clay	AQ/SOLV	Solid	100
9	Minugel®	AR	Attapulgite Clay	SOLV	Solid	100
9	Minugel®	LF	Attapulgite Clay	AQ/SOLV	Solid	100
9	Minugel®	200, 400	Attapulgite Clay	AQ/SOLV	Solid	100
12	Zeothix®	177 & 265	Precipitated Silica	AQ/SOLV	Solid	100
16	Hi-sil®	T-600 & T-700	Precipitated Silica	AQ/SOLV	Solid	100
16	Hi-sil®	200	Fumed Silica	...	Solid	100
16	Hi-sil®	M5	Fumed Silica	...	Solid	100
17	Benaqua®	4000, 8000	Hectorite Clay	AQ	Solid	100
17	Bentone®	27, 34 & 38	Organoclay	SOLV	Solid	100
17	Bentone®	SD-1, 2 & 3	Organoclay	SOLV	Solid	100
17	Bentone®	EW	Smectite Clay	AQ	Solid	100
17	Bentone®	LT	Bentonite Clay	AQ	Solid	100
20	Aquamont®	600	Modified Bentonite	AQ	Solid	100
20	Bentolite®	...	Purified Bentonite	AQ	Solid	100
20	Claytone®	Series	Organo-mod. Montmorillonite	SOLV	Solid	100
20	Laponite®	Series	Synthetic Hectorite Clay	AQ	Solid	100
20	Lapomer®	40	Laponite Clay + Org Polymer	AQ	Solid	100
21	Troythix®	A-SS	Organoclay	...	Solid	100
21	Troythix®	A-S	Silicate	...	Solid	100
24	Tixogel®	VP & VZ	Organoclay	SOLV	Solid	100
24	Tixogel®	LX	Organoclay	AQ	Solid	100
25	Van gel®	B	Refined Colloidal Clay	AQ	Solid	100

clays is attapulgite, which is chemically described as hydrated magnesium aluminum silicate. The lath-shaped particles of this mineral as supplied are colloidal (less than 0.5 μm), and the crystal structure is chain-like. In an aqueous environment, attapulgite is nonswelling and essentially inert. Thus, coatings containing attapulgite clay thickened not by swelling, but instead by the structured reflocculation of the pigment particles into a colloidal interaction network after shearing. In coating preparation, attapulgite clays can be added as powders or as pregelled dispersions throughout the formulation process. However, they are normally added in the grind using high-speed mixers for dispersion and hydration. The thickening power of these clays is high, and salts have little or no effect on viscosity. However, like many other ITRMs, the amount of attapulgite clay required for thickening is generally higher than for organic TRMs, and the water demand is high (water is pulled from the aqueous phase to wet the particle surface, thereby increasing effective coating solids).

Bentonite Clays

Bentonite clay is obtained from the mineral montmorillonite (a Fuller's earth mineral), which is described as an aluminum silicate with varying degrees of aluminum replacement with magnesium, calcium, and sodium. The crystal structure is a three-layer sheet which forms flake-like colloidal particles of less than 0.5 μm. In aqueous media, bentonite is naturally hydrophilic and readily dispersible. The water is taken up between the mineral laminae, causing the lattice structure to stretch and swell. Thickening is due to a combination of swelling and particle network interaction, and purified forms of unmodified bentonite are highly effective as thickeners in aqueous coatings. Although the thickening mechanism is rather different than that of attapulgite clays, most bentonite clays also require wetting, high-shear for dispersion, and time for complete hydration. Some modified grades are, however, readily dispersible with conventional agitators. For effective incorporation, pH must be carefully regulated. If it is too high, excessively rapid hydration occurs, and if it is too low, hydration times are long with loss in thickening efficiency. The presence of salts (electrolytes) may cause flocculation, rendering bentonite ineffective in highly ionic environments.

Organoclays

Many different grades of organoclays are available for both solvent-borne and aqueous coatings. Although these products differ in modification, the mechanism for thickening and rheology control is substantially the same. Bentonite clay is one of the principal minerals used to prepare organoclays, and, being both hydrophilic and oleophobic in its natural form, it must be modified for dispersion in organic solvents. Only after a sophisticated purification process followed by cation exchange with organic ammonium bases is the surface rendered sufficiently organophilic for use in nonaqueous media. As supplied, organoclay thickeners are in the form of agglomerated platelet stacks. Conventional organoclays require wetting and shear for deagglomeration and the addition of a chemical polar activator for full rheological development. The chemical activator serves to disperse the organoclay and also carries water into the hydrophobic organic solvent to insure full hydrogen bonding. Some newer products still require wetting and shear but are functional without the chemical polar activator. Although not essential, elevated temperatures are preferred for efficient processing. High-performance organoclays have recently been developed with greater thixotropy and improved sag resistance [*62*].

Special grades of organoclays (organophilic clays) have also been designed for aqueous coatings. Some of these depend on shear, wetting, and hydration for full rheological performance, while others are available in readily activated slurry form. The efficiency of these products is generally independent of pH [*63*].

Synthetic Silicas

Another class of inorganic thickeners are certain types of synthetic amorphous hydrophilic and hydrophobic silicas. Both are widely used in solvent-borne coatings; however, excessive hydration generally limits the utility of the hydrophilic silicas in aqueous media. Two forms of amorphous hydrophilic silica are commercially available and get their names, "precipitated silica" and "fumed silica," from the manufacturing processes. A proposed thickening mechanism for these silicas is based on hydrogen bonding between the silica particles and with other coating components to form a three-dimensional structure. High water demand may also contribute to thickening with these products.

Precipitated Silica

Precipitated silica is obtained in a wet process by the neutralization of sodium silicate solution. This results in a polar, fully hydroxylated surface. Consequently, hydrogen bonding is strong, and excellent thickening comparable to that of fumed silica is obtained especially in nonpolar media. However, because of the competition between hydroxyls on the silica and those in the continuous phase, precipitated silica tends to be less efficient than fumed silica in polar (for example, aqueous) media.

Fumed Silica

Fumed silica is fumed silicone dioxide which is prepared by hydrolysis of silicon tetrachloride vapor in a hydrogen-oxygen flame. The product gets its name from the smoke-like appearance as it forms in the flame. In the fuming process, a partially hydroxylated surface containing silanol, siloxane, and hydroxyl groups is generated, which is somewhat less polar than that of precipitated silica. pH does have a significant effect on the thickening efficiency of fumed silica in aqueous systems. To be effective, pH must be below about pH 7.5. Above this pH, electrostatic repulsion keeps the particles far enough apart to inhibit hydrogen bonding.

Organosilica

Hydrophobic silica is produced when freshly manufactured hydrophilic fumed silica is treated with organosilane or organosiloxane compounds [*64*]. This is a chemical modification in which many of the surface hydroxyl groups are replaced with organic functionality. After treatment, these products have minimal surface silanol groups left for hydro-

gen bonding, and the amount of carbon incorporated into the fumed silica (on the surface) is typically on the order of 1 to 5%. Hydrophobic silicas are generally superior to hydrophilic silicas in water-reducible systems; however, order of addition can be important.

ORGANIC TRMs FOR SOLVENT BORNE COATINGS

Besides the inorganic products described above, a variety of organic additives also function as thickeners, rheology modifiers, and thixotropes in solvent-borne systems. These products are mostly available in liquid paste and powder form. Many require some dispersion and activation for thickening, and the recommended process temperatures often depend on the strength of the solvent present in the coating formulation. Careful formulation procedures are required to avoid seeding, "false body," or loss in thickening efficiency. Among the many types of organic products available for use as thickeners and flow control agents for solvent-borne systems are castor oil derivatives [*62*], modified acrylic copolymers, polyethylene glycol, polyamides [*65*], polymerized oil derivatives, organic esters, complex polyolefins, and aramid pulp fibers [*66*]. Because of the number of products, their diverse nature, and the fact that little information is available on many due to their proprietary status, no attempt will be made here to classify or categorize these products and their suppliers. Resources for this information are available elsewhere (for example, see McCutcheon's Functional Materials in the Bibliography).

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LIST OF PRODUCERS AND SUPPLIERS

*Company Reference Numbers for Tables 3, 5, and 6

1. Alco Chemical Corp., Div. of National Starch & Chemical, 909 Mueller Dr., P.O. Box 5401, Chattanooga, TN 37406-0401.
2. Aqualon, 1313 N. Market St., P.O. Box 8740, Wilmington, DE 19899-8740.
3. Cabot Corp., Cab-O Sil Division, P.O. Box 188, Tuscola, IL 61953-0188.
4. Crosfield Co., 101 Ingals Ave., Joliet IL 60435.
5. Degussa Corp., Pigments Div., 425 Metro Place North, Dublin, OH 43017.
6. Dow Chemical USA, Larkin Lab, 1691 N. Sweede Rd., Midland, MI 48674.
7. Dry Branch Kaolin Co., Kaopolite Inc., R.R. 1, P.O. Box 468-D, Dry Branch, GA 31020-9798.
8. Engelhard Corp., Specialty Minerals and Colors Group, 101 Wood Ave, Iselin, NJ 08830-0770.
9. Floridin Co., 1101 N. Madison St., Quincy, FL 32351.
10. B. F. Goodrich Co., Specialty Polymers & Chemicals, 9911 Brecksville Rd., Brecksville, OH 44141.
11. Henkel Corp., Functional Product Grp., Coatings & Inks, 300 Brookside Ave., Ambler, PA 19002.
12. J. M. Huber Corp., Chemicals Division, P.O. Box 310, Havre de Grace, MD 21078.
13. Hüls America Inc., 80 Centennial Ave., P.O. Box 456, Piscataway, NJ 08854.
14. Kelco, Division of Merck & Co. Inc., 8355 Aero Dr., San Diego, CA 92123.
15. Pfizer Chemical Div., 235 E. 42nd St., New York, NY 10017.
16. PPG Industries, Specialty Chemicals Bus. Unit, 3938 Porett Dr., Gurnee, IL 60031.
17. Rheox Inc., P.O. Box 700, Wyckoffs Mill Rd., Hightstown, NJ 08520.
18. Rhone-Poulenc Corp., Colloids Div., 1525 Church St., Marietta, GA 30060.
19. Rohm and Haas Co., Rohm and Haas Building, Independence Mall, West, Philadelphia, PA 19106.
20. Southern Clay Products Inc., Division of Laporte Absorbents, 1212 Church St., P.O. Box 44, Gonzales, TX 78629.
21. Troy Chemical Corp., P.O. Box 366, 72 Eagle Rock Ave., East Hanover, NJ 07936.
22. Union Carbide Chemicals and Plastics Co., UCAR Emulsion Systems, 410 Gregson Dr., Cary, NC 27511.
23. Union Carbide Corp., Specialty Chemicals Division, 39 Old Ridgebury Rd., Section H-2375, Danbury, CT 06817-0001.
24. United Catalysts Inc., Rheologicals and Performance Minerals Group, subsidiary of Süd Chemie AG, P.O. Box 32370, Louisville, KY 40232.
25. R. T. Vanderbilt Co, Inc., 30 Winfield St., Norwalk, CT 06855.

Part 8: Physical Characteristics of Liquid Paints and Coatings

31

Density and Specific Gravity

by Raymond D. Brockhaus[1]

INTRODUCTION

Why Concern Ourselves with Density?

The World of the Producer and the Customer

MATERIALS ARE EXCHANGED FOR AN agreed-upon value based upon a "cost per unit material." The "unit of material" is in terms of what the user wants to do with the material expressed in physically measurable units such as volume or weight. The customer does not want to be shorted, and the provider does not want to give away material. Accurate measurements are expected to keep both parties happy. When a customer wants a gallon of paint, the manufacturer blends the component materials together by weight and fills out by weight. Balances are easy devices to place and use with filling lines. Delivery of constant volumes, on the other hand, is not an easy task, as will be explained later. Measurement of the weight of a known volume of the paint generates a relationship defined as density. With this relationship, the producer can fill by weight and then sell to the customer on a by volume basis. The customer wants volume; the producer wants to work in weights. The relationship—density—enables the transformation to make life easier for both groups.

Measure of Quality

In the open marketplace, the business person and the customer have this rule of thumb—let the buyer beware. Testing for quality of the shipment is best done on-the-spot, quickly, and in a way that is highly reliable. If you are in charge of the wine and ale stocks of a restaurant, one method of determining the quality of the goods obtained would be verification of the density with flotation probes called hydrometers. Similarly, the purchasers of metals such as gold, lead, silver, and copper could use various methods of determining density to keep from being cheated and assuring quality.

In our more modern world, with instruments capable of assaying individual chemical compounds in complex mixtures, verification of density has become a manufacturing tool for in-process control. Density measurement becomes an indirect assurance that the ingredient(s) of interest exists in the material of exchange at the proper concentration. For paint, ingredients such as solvents, polymers for binders, and pigments have a different range of density typical of that material. Partial omission of a major component, for example, a solvent, can make the paint density change from the formula loading target. Quick approximate estimations of density can be done with inexpensive equipment that acts as a screening tool, catching special-cause errors like wrong material shipped. Common-cause errors of minor contamination are usually not caught this way.

The use of density measurements as a measure of quality is declining in favor of testing tuned to providing measurements of ingredient concentrations and chemical functionality. This is most often a balance between spending time, money, and manpower on testing and risking the liability of inadequate product performance.

Regulatory Concerns

In addition to customers and producers, government can express concerns in the exchange of materials. Government's concern is for regulation. Paints or other similar heterogenous materials are mixtures in which only the nonvolatile portion of the bulk material being exchanged is of true value to the customer. The "carrier" portion of the bulk material must be accounted for because it is a discarded material and thus a "pollutant." The carrier portion, solvents, and viscosity reducers are used to aid in transporting the solids to the work surface to form a thin film. These pose disposal problems and impact landfills, air and water quality, which are under government regulations. Paint volume solids and critical pigment volumes are two significant concepts which must be understood and accounted for when dealing with modern government regulations [*1*].

Definitions—Density—Static and Dynamic Mathematical Models

Static Model

Density is the weight in vacuo, that is, the mass of a unit volume of a material at any given temperature [*2*]. In vacuo is specified because measurement of weights in gaseous or liquid environments may require a buoyancy correction. If the volume of the mass being weighed is large, a correction must be made for displacement of the environmental media (air or a liquid).

For some samples, however, vacuum conditions will cause vaporization of the sample. Therefore, "in vacuo" is usually a theoretical condition rather than a normally experienced one and deals with the surrounding environment. The balance used to weigh the sample must also be in vacuo.

The Greek letter ρ (rho) is used to denote density.

$$\rho = (m/V) \tag{1}$$

[1]Research Associate, E. I. Du Pont, Automotive Products, 400 Groesbeck Highway, Mt. Clemens, MI 48043.

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where m is mass, and V is volume expressed in units consistent with the mass units.

$$\rho = (W/V) \tag{2}$$

where W is weight (a function of mass), and V is volume expressed in units consistent with the mass units.

Dynamic Model

Density is a mathematical value describing a balance of physical forces acting on a material called mass occupying a known volume of space under known temperature conditions. This equation is identical to that given in the static model. Density is expressed as a single value, but is really an average value of forces dynamically fluctuating, both internal to the material and external as the surrounding environment.

Two definitions are included here. The first (static) is the traditional model. It has changed only slightly over the ages, being upgraded with the terms "mass" in place of weight and "in vacuo" after vacuum bell jars were developed. The second (dynamic) is a more fundamental model, dealing with materials on a molecular level, where the concepts of chemical functionality, kinetic and potential energy, and interfacial boundaries come into play. With the second model, we can understand and deal with mixtures of chemicals and mathematically deal with how a single component's densities interact when mixed.

The attractive forces exerted on a primary mass or collection of particles by a second mass much larger than the first mass is called *weight*. This is an attractive action, resulting in compression and increasing the density of the primary mass. The dispersing forces are caused by thermal energy absorption, resulting in particles of increasing motion or kinetic energy. This manifests as temperature of the material.

The volume of space occupied by a mass of particles that exists at an average kinetic energy level expressed as the temperature of the physical material is the *volume*. This includes the voids of space between the particles on a molecular level.

The average kinetic energy level of the material is expressed in the motion of the particles of the material. Material is made up of many small particles that are independent in their motion. These motions are random, such that the overall motion in the X, Y, and Z directions cancel each other and the net motion of the total mass is zero. As the kinetic energy level, expressed as temperature, increases, the distances between particles increase and the material is identified as expanding.

Special cases used as standard measurement reference points:

- One cubic centimetre (cm^3) of pure water (H_2O) at 4.0°C is defined to weigh 1.0000 g.

$$\text{Density}_{\text{water}} = 1.000\ \text{g}/1.000\ \text{cm}^3$$

- 1.000 mole of a gaseous compound occupies 22.4 L of volume at 0°C (273°K) at 1.000 atmosphere pressure (a molar volume).

For air, whose composition is 22% by weight oxygen and 78% by weight nitrogen (ignoring other gases), 1 mole weight = (32 g × 0.22) + (28 g × 0.78) = 28.88 g. Density = 28.88 g/22 400 cm^3 = 0.001 29 g/cm^3 or 1.29 g/L [*3*].

Relative Density, also referred to as specific gravity, is the ratio of a density determined for Material A at Temperature T_1 divided by the density of a reference material at some temperature, T_2. For solids and liquids, the reference material is pure water. For gases, the reference material is air.

$$\text{Density}_{\text{Relative A}} = \frac{\text{Determined Density A at } T_1}{\text{Determined Density Water at 0°C}} \tag{3}$$

If a Liquid A has the same density as water at T_1, when determined by a bouyancy device, then the density can be determined from a table of known density values established for pure water over a range of temperatures.

When T_2 equals 4.0°C, the relative density for pure water equals the measured density. As temperature increases, water expands. For a constant volume, the mass of water must be decreased to fit into a given volume. Thus, water's density value must decrease with increasing temperature. Relative density is a ratio of two values carrying the same units. Therefore, relative density is a unitless number.

Specific Gravity—An old term; the term *relative density* is identical and is less misleading [*4*].

Apparent Density—A density value for powders and macroscopic particulate solids which are compacted by vibration. Air is still present in the voids between the particles and in pockets or voids at the irregular surface of the macroscopic particles. This means the volume is greater than just for the solids, and the density is smaller in value than if the material was a liquid or compacted such that no voids existed. Pigments used in paint are mechanically worked with solvents and resins to fill in these voids. The *true density* of the pigment, which is needed in paint calculations, is that obtained without any of the air (void) contribution.

Fundamental Concepts—Material, Objects, Volumes, Masses, and Weights—What Really is Density?

Density is more than just the mathematical numerical value identified above. It also incorporates units of measure which are, in turn, based upon more general and fundamental concepts. These units of measure assume a set of definitions which will be explored in very general terms. These

TABLE 1—Density of water, grams per cc [*2*].

Temperature, °C	Density, g/cm^3
15	0.999 099
16	0.998 943
17	0.998 744
18	0.998 595
19	0.998 405
20	0.998 203
21	0.997 992
22	0.997 770
23	0.997 538
24	0.997 296
25	0.997 044
26	0.996 783
27	0.996 512
28	0.996 232
29	0.995 944
30	0.996 565 6

units are crucial to understanding the dynamic model of density and in allowing microscopic concepts to be explored.

Material—Anything (a physical entity) which exists for a duration of time, occupies space, and has mass. Mass is a stable configuration of atoms individually loosely organized as elemental atoms or joined together chemically to form molecules.

Object—A collection of materials, homogeneous or heterogeneous, localized to a portion of volume (space). The material can be in any one of three states: solid, liquid, or gaseous. The shape of the volume of space occupied by the object plays a role in dealing with density but does not define the object itself.

Volume is based upon measurement of distance in three directions at right angles to each other as in Fig. 1.

The physical universe in which we live is often described in three dimensions in terms of distance, which is a scalar property. When dealing with three dimensions, the term *distance* is described as length, width, and depth. An object having all three is described as having *volume*. The mathematical value for volume is the product of multiplication of the three scalar values. Volume can exist without objects occupying that space. This condition is called a vacuum. Vacuum's volume and object's volume can both be of very irregular and nonmatching shapes, yet they can equal in the scalar value of the volumes. Examples are shown in Fig. 2.

Problems with Volume Measurements

Customers often make use of material based on volume as applied and want to purchase these products in containers recognized to hold standard volumes. Materials have the property of responding to temperature changes with expansion or contraction of their volume. Products that experience wide temperature ranges during filling, shipping, storage, or in use must also have extra unfilled volume to accommodate expansion or the material forces leak and material is lost. This problem is most severe with liquid materials. Material suppliers use containers with larger than exact volume required to allow for expansion. These vessels must be marked in some way to indicate the volume increments if they are to be used for filling by volume. Producers seldom can or want to control temperature during packaging. Temperature control devices will add expense without making a difference in the material's performance. Without temperature control, filling at a constant volume will produce units of varying amounts of material. Use of density overcomes these problems and permits correct volumes to be filled out.

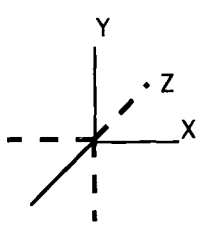


FIG. 1–Coordinates in three dimensions.

Weight and Mass

A fundamental attribute of a physical entity is *mass*. This is one of the indefinable mechanics [*4*]. Two physical objects exhibit an attraction for each other in proportion to the quantity of mass in each object. The greater the mass, the greater the attraction. When the ratio of two masses is grossly unequal, such as the planet Earth and an object on its surface, the larger mass is assumed to be constant and the second object is described to have a "weight" relative to this larger object. The mass of the planet is effectively unchanging and thus constant. Our moon is also a very large object, but smaller than the earth, thus its attraction to a second object would be weaker than for the Earth. Mass is the unchanging, fundamental property.

But we are human, and we deal in the measurement of weight, which is a force. While weight is a vector quantity having both scale and direction, the direction portion is taken for granted and weight is usually treated as only a scalar value. Figures 3 and 4 graphically depict this issue.

Weight, w, is defined as a force of gravity, F_g, [*4*].

$$w = F_g = G\frac{mm_E}{R^2} = mg \tag{4}$$

where

G = a gravitational constant for Earth = 6.670×10^{-11} N·m²/kg m²,
m_E = mass of the Earth = 5.98×10^{27} g, and R is the radius of the Earth = 6370 km,
m = mass of a second body (Newton's law) [*5*],
g_E = 9.80 m/s² or 32.0 ft/s², and
g_{Moon} = 5.333 ft/s² or ⅙ that for Earth.
$g_{\text{Distance from Earth}} = 1.0 \times 10^6\,\text{km} = g_E/[(1.0064 \times 10^6\,\text{km})^2/(6370\,\text{km})^2] = 0.004\,g_E$

These values are given as constants in physics calculations but actually represent average values. In the real world, the value of g varies from location to location for a variety of reasons. Table 2 and Figs. 5 and 6 about mountains and dense buried masses of rock demonstrate this.

Example 1: A gallon of paint produced in Galvaston, Texas has a weight of 10.000 lb/gal. The product finds its way to

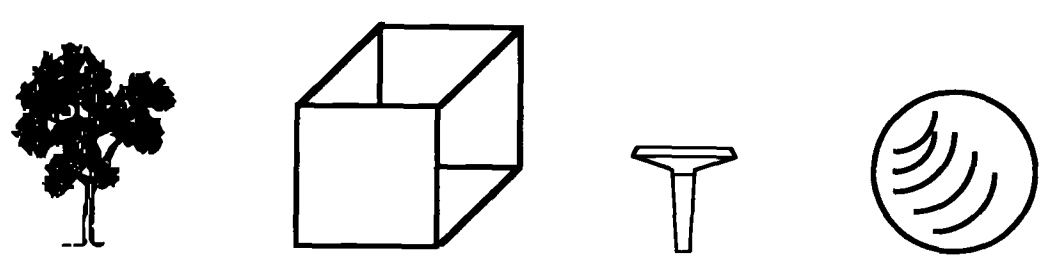


FIG. 2–Examples of physical objects.

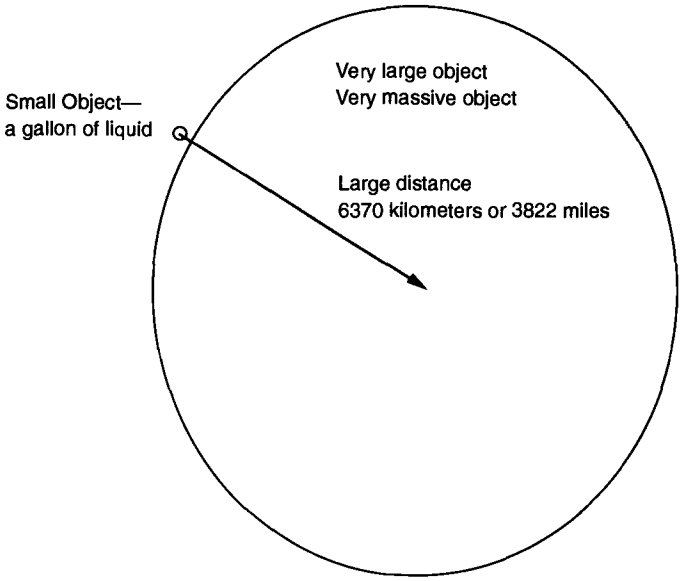


FIG. 3–Moderate distance to large body center.

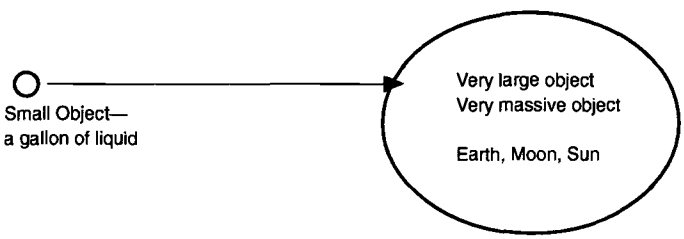


FIG. 4–Vast distance to large body center.

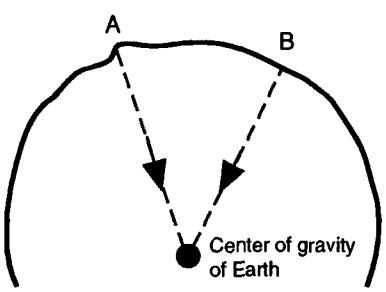


FIG. 5–Height effects on objects on the earth's surface. From *The New Book of Popular Science*, 1993 Edition. Copyright 1993 by Grolier Incorporated. Reprinted by permission.

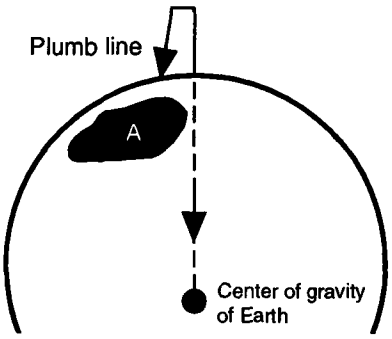


FIG. 6–Large buried mass concentration effects on objects on the earth. From *The New Book of Popular Science*, 1993 Edition. Copyright 1993 by Grolier Incorporated. Reprinted by permission.

Eagle City, Alaska. Here it has a gallon weight of 10.03 lb/gal. The difference is minor but real. If the paint specification is a density in the range of 9.90 to 10.10 lb/gal, the +0.03 lb leaves only 0.07 lb for testing errors before the material is identified as out of specification. As environmental regulations on the volatile organic content (VOC) increase in importance, these minor differences will play a larger role and should not be overlooked for their contributions to relationships such as density.

The pull of gravity is not as strong at a mountaintop, A, as it is on the plain, B. The reason is because A is at a greater distance from the center of gravity than B. The plumb line in Fig. 6 does not point exactly to the earth's center of gravity because it is attached to A, which is a dense part of the earth's crust [*5*].

Example 2: The weight of a gallon of paint in New York City is recorded at 9.5 lb. The distance from the center of the Earth is 6370 km at this location. At a distance of one million kilometres from the earth, the same gallon of paint would weight 0.003 78 lb.

Has the amount of mass changed? No. Has the weight changed? Yes, because of distance. Has the volume of the material changed? Possibly. If the gallon container is surrounded by air at 1 atm, the container shape is retained and the material in it will not overflow. But, in the new location, the fluid does not want to remain together. It forms droplets and wants to float off in all directions. It has lost the cohesiveness provided by gravity. Has the density of the material changed? By definition, yes, drastically! By fact, little. The same physics rules apply in both locations, but the environment has changed and with it our appreciation for the term *mass*.

TABLE 2—Values of *g*, the acceleration due to gravity [*5*].

Place	Value[a]	Place	Value[a]
Cambridge, Massachusetts	980.398	Denver, Colorado	979.609
Eagle City, Alaska	982.183	Galveston, Texas	979.272
Greenwich, England	981.188	Honolulu, Hawaii	978.946
Madras, India	978.281	New Orleans, Louisiana	979.324
Panta Delgada, Azores	980.143	Reykjavik, Iceland	982.273

[a]Centimetres per second per second. Use of centimetres emphasizes the differences which are occurring in the second through sixth numerical place.

Example 3: A 1.00 m^3 Styrofoam cube of material is created on earth in our atmosphere (air) at 20°C and 1.0 atm. This is a heterogeneous material because it has trapped air in the foam. Let's say it weighs 900 g on a balance on an open desk top.

$$\text{Density}_{\text{earth}} = 900\,\text{g} \div 1.00\,\text{m}^3 = 900\,\text{g/m}^3$$

Next, this cube is taken to the moon (gravitational factor = ⅙ Earth) and kept inside a building with 1.0 atm at 20°C.

$$\text{Density}_{\text{moon}} = (900\,\text{g} \times \tfrac{1}{6} \div 1.00\,\text{m}^3) = 150\,\text{g} \div 1.00\,\text{m}^3 = 150\,\text{g/m}^3$$

Next, the cube is taken out onto the moon's open surface, where there is no atmosphere (vacuum conditions).

Now, two things happen to this cube.

1. There is no air to displace when weighing the cube. It can thus exhibit a heavier weight since there is no buoyancy correction: 1 m^3 of air weighs 1.29 g on Earth and 0.215 g on the Moon. So the weight would be 150.215 g.
2. The material can also lose the air entrapped in the foam. This may be a slow process, but it can happen. Now the cube will appear to lose weight. Let's say it loses 0.050 g by moon weight and now weighs 150.215 − 0.050 g.

$$\text{Density}_{\text{vacuo,moon}} = 150.165\,\text{g} \div 1.00\,\text{m}^3 = 150.165\,\text{g/m}^3$$

Return the cube back into the building on the moon with 1.0 atm and the weight might now be 149.95 g if the foam structure is strong enough to retain the cubic shape without crushing from the external pressure. Its density is now 149.95 g/m^3.

Density is a very simple, straightforward concept and relationship. Still, as noted before, physical reality can and does impact on it, adding subtle perterbations that should be understood. What appears to be homogeneous may not be. Physical reality is a source of variability, and affects must be taken into consideration when arriving at results we will share with one another.

Solids, Liquids, and Gases—As Concepts and Under Ideal Conditions

Materials exist in one of three states: solids, liquids, or gases. For an equal amount of weight, solids usually occupy less volume than liquids, which occupy much less volume than a gas. Solids also retain a shape and flow or distort very slowly. Liquids take on the form of a containing vessel. Gases have no shape and are bounded and shaped by their container. Techniques exist to determine densities for all three states.

Solids—Figure 7 is a depiction of a solid in which the particles are atomic or molecular in scale. The distance between particles is a regular, repeatable distance. Most kinetic energy is gone. Only external pressure can shorten the distance between particles. This shortening is called compression and affects the ratio of weight present and the actual volume occupied by that mass of material. If the solid remains compressed after the external pressure is released, the material is called inelastic. If it returns to the original volume, it is elastic. Density of solids can depend on the processing history.

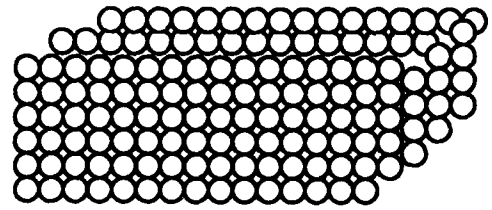


FIG. 7–Simple model of particles of matter in solid state.

Liquids—In a liquid as depicted in Fig. 8, the particles are molecular or atomic in scale. Distances between particles are not constant. Kinetic energy is greater than in solids. External pressure can shorten the distance between particles. Each material has a characteristic compressibility factor. All liquids behave elastically, flowing back and filling in. The population of particles has a distribution of kinetic energy values, with some being greater than the surface energy. The portion of the population which has a kinetic energy greater than the surface energy escapes and is called *vapor.*

For ideal conditions and "conceptual" materials, no interactions occur between the materials, the testing containers, and the surrounding environment. The material investigated is well behaved. When such materials are mixed together, the weight of each material times the individual material's density will add together as a linear sum.

Gases—In a gas, as depicted in Fig. 9, the particles are molecular or atomic in scale but more widely separated. Distance between particles is irregular. Kinetic energy is even higher than in liquids. External pressure can shorten the distance between particles. Each material has a characteristic compressibility factor.

Weighing solid or liquid material in a container or as a solid object is an easy task. Instruments for this task keep improving in accuracy, precision, ease of use, and lower cost.

For gas-phase material, vessels of accurately determined volume can be purchased and used. Materials of construction for durability and reuse are of concern. If the temperature of testing is controlled within the tolerance of the calibration of these vessels, expansion is not a concern. Since gases are seldom incorporated into a paint system, this topic will be passed over.

Further Discussion of Liquids and Solids

For liquids, containers can be constructed to hold a known volume. These vessels can be mass produced with adequate

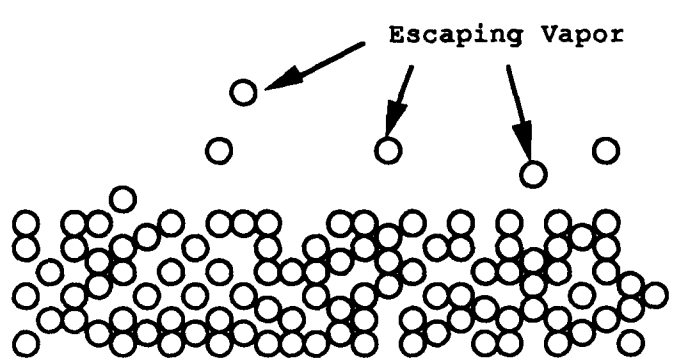


FIG. 8–Simple model of particles of matter in liquid state.

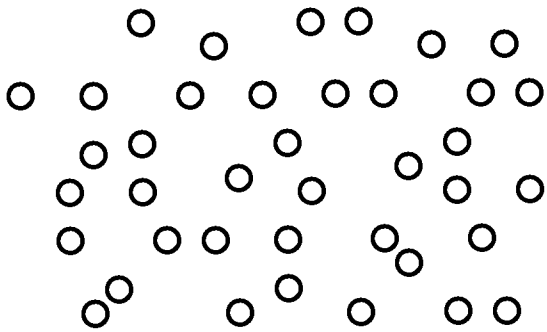


FIG. 9–Simple model of particles of matter in gas state.

accuracy to allow large numbers of users to have access. These are called *liquid pycnometers*. Some are also called *gallon weight cups*. Within the temperature range of 1°C and 99°C, the density of water can be determined. More detail will be given in the section entitled "Liquids." Devices that can float in water can be calibrated to show a scale calibrated directly in density. When these floats are used along with a scale for weighing, the volume of material can be determined [*6,7*].

Figure 10 contains drawings of several pycnometers as seen in a commercial scientific supplies catalog. The catalog text descriptions for two pycnometers have been included to inform you as to sizes, capacities, materials of construction, etc. The features discussed identify attributes of importance to the end user.

Liquids have other properties that can be used to test for density. One of these is sound transmission. Replacement of air with a liquid in a container will cause that container to shift a tone impulse to higher frequencies. The extent of the shift is related to the liquid's density and can provide a direct measurement with different degrees of accuracy depending on the sophistication of the instrument.

For solids, the task is more complex. Two paths are available. Either shape the solid into a known geometric figure and calculate the volume or use the solid to displace a material such as a liquid or a gas which has a known density. The solid can be shaped by mechanical, thermal, or chemical means. Mechanical means can be employed to cut, carve, and shape, then weigh. Thermal shaping is changing the solid into a liquid using heat to melt the solid, pouring the liquid into a mold, cooling to form a solid, and then weighing. Chemical shaping is dissolving the solid in a "carrier" liquid (solvent), pouring the solution into an open mold, and evaporating the solvent, leaving behind a solid property shaped to accommodate testing. The drawbacks of this technique are:

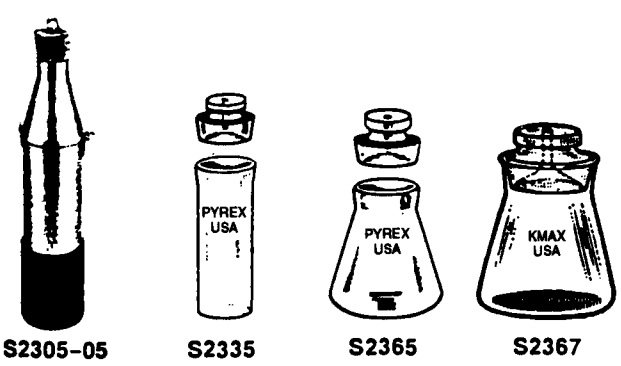
1. Complete solvent removal is often difficult.
2. Chemical reshaping of solids can cause problems if the original solid had small air pockets or if the solvent used is trapped in these voids, thus actually changing the solid and affecting its apparent density. Solids which demonstrate the latter behavior have a bulk density different than their skeletal density.

The principle of buoyancy, discovered in the third century by Archimedes, provides a means to determine volume [*5*]. Determination of volume by displacement requires acquiring a weight in air and a weight in a liquid of known density at the testing temperature. Complete submersion of the solid object or a representative portion of the material in a liquid of known density is required while determining the material's apparent weight. See Fig. 11. The weight difference is equal to the weight of the volume of liquid displaced. Knowing the liquid's density and the weight difference, the volume for the tested portion can be calculated by the following formula:

$$g_{\text{Distance from Earth}} = 1.0 \times 10^6\,\text{km} = g_E \frac{(6370\,\text{km})^2}{(1.0064 \times 10^6)^2} = 0.004\,g_E \quad (5)$$

Solids, Liquids, and Gases as Concrete Materials in a Physical World

A vast variety of materials exist, and interactions are possible between any of the different types of materials. When an



ASTM Crude and Fuel Oil Sampler

As specified in ASTM D270 for sampling light lubricating and crude oils, nontransparent gas oils, and fuel oils in sewage tanks. Copper with 19 mm (0.75 in.) diam neck opening and 430 cm (17 in.) brass handle; body ODxH, 95x356 mm (3.75x14 in.); capacity, 950 mL (1 qt).

S2305-05 .....

PYREX® Hubbard-Carmick Specific Gravity Bottle (Corning No. 1620)

■ Ŧ Stopper, ASTM

For use in place of S2335 in accordance with ASTM D70; especially for viscous fluids and semisolid samples. Conical shape with wide bottom for increased stability and ground solid stopper, concave on bottom. Capacity, 25 mL; bottom diameter, 40 mm; diameter of mouth, 25 mm; height without stopper, 45 mm; weight empty, less than 40 grams. With 24/12 short length Ŧ grinding and 1.6 mm hole in stopper to allow air to escape.

S2365 .....

FIG. 10–Specific gravity testing—pycnometers. (Courtesy of Sargent-Welch).

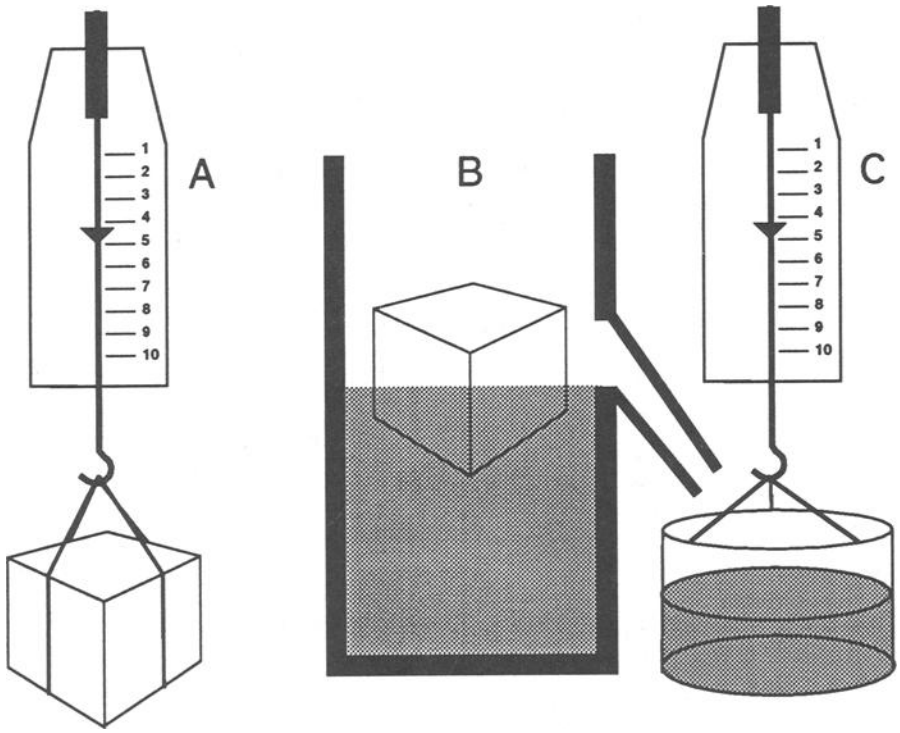


FIG. 11—*Displacement technique*—A block of wood weighs 5 oz (*A*). The wood block is placed in an overflow can filled with water up to the spout (*B*). The displaced water flows into the container at the side of the can (*C*). The weight of the displaced water equals the weight of the block if the block's density is less than or equal to the water. If the density of the block is greater than water, the entire volume of the block is displaced and the weight of the *water* equals the volume of the block (if temperature = 0°C) [*5*]. From *The New Book of Popular Science,* 1993 Edition. Copyright 1993 by Grolier Incorporated. Reprinted by permission.

attribute, like density, can be directly measured, it is possible to identify two types of these interactions. The first is *ideal* behavior with respect to the attribute under investigation and the amount of mass used. These interactions are well behaved and produce predictable attribute changes. The second type is *nonideal* and means that other interactions are taking place than just that of mass-to-mass attraction. Materials are ideal if when mixed together the sum of the weight fraction of each material times the material's density equals the density determined for the entire mixture. Materials are nonideal if when mixed together the sum of the weight fraction of each material times the material's density does not equal the density determined for the entire mixture.

Some solids can exist with varying degrees of crystallinity incorporated into their solid form. As temperatures cycle up and down in the surrounding environment of these solids, the solids will change density as their degree of crystallinity changes and they move toward a thermodynamically stable form of the solid.

Finally, materials can chemically interact when mixed, producing or absorbing heat and generating an entirely new material with its own unique attributes.

These actions are not bad or good, but they basically exist and must be taken into consideration when dealing with mixtures such as liquid paints and solid coatings.

When a material (A) is homogeneous, the density is a fixed value for a fixed temperature. When a material (B) is heterogeneous, the density is also a fixed value for a fixed temperature. When two different materials, homogenous or heterogeneous, are mixed together, they become a new, heterogeneous material, and the resultant density is a new fixed value for a fixed temperature. Depending on whether the interactions are ideal or nonideal, the density can be predicted by calculation or a deviation in the density will result. Paints are formulated as ideal mixtures, but they don't always follow this assumption. The relationships between these values are given below [*8*].

$$A + A \text{ has A's density which is } \frac{W_A\rho_A + W_A\rho_A}{W_A + W_A} \quad (6)$$

$$B + B \text{ has B's density which is } \frac{W_B\rho_B + W_B\rho_B}{W_B + W_B} \quad (7)$$

$$A + B \text{ has a new density which may be } =, >, \text{ or } < \text{ that of } A \text{ or } B \text{ and is } \frac{W_A\rho_A + W_B\rho_B}{W_A + W_B} \quad (8)$$

where

W = weight of component,
ρ = density of the component.

Many important materials are available as complex mixtures in today's world. These mixtures can be heterogeneous in terms of phase. Gasoline for the car and lawn mower can contain butane dissolved into the heavier hydrocarbons. Paints, inks, and cements contain liquids and solids, with the liquid phase either neutral or reactive. If the liquid's role is

neutral, it can be a solvent or carrier or plasticizer. If the liquid's role is reactive, it is called a binder, reactive diluent, or catalyst.

Modern paints contain chemically reactive, low-molecular-weight polymers that, when heated, produce a crossed-linked solid and usually volatile by-products. When chemical changes occur, the linear density addition model is correct only by chance. Usually the volume is reduced from chemical bonds forming, and as a result, the density goes up.

Theoretical volume solids have been calculated for years in the coating industry using the linear model. This worked well for lacquers, varnishes, and other systems where chemical reactions took place at low levels and were of the oxygen uptake type, making the final film heavier from oxygen addition. Modern paints react internally, generate by-products of low molecular weight, and actually lose weight during cross-linking and film formation. But, because there has been no good way to determine the volume of paint films that is repeatable and reproducible, the practice of calculating volume solids is still used in the 1990s. (*Repeatable* means in the same lab, with the same instrument, time after time, and *reproducible* means between different sites or labs using similar but physically different instruments like balances, ovens, etc.)

Definitions Related to Density and Specific Gravity

$$\text{Bulk Density} = \frac{\text{Total weight of object including air or water}}{\text{Total volume occupied including air or water}} \quad (9)$$

$$\text{Skeletal Density} = \frac{\text{Total weight of object less air or water}}{\text{Total volume of actual material less air or water}} \quad (10)$$

Surface interactions—These interactions involve wetting of solid surfaces by liquids during liquid displacement testing. In determining the volume of a material due to displacement of a liquid, the liquid must come in close contact with the material surface. When the liquid meets or wets the surface without penetration into the bulk of the material, the volume of liquid displaced is equal to the bulk volume of the material being tested. When the liquid does not contact and wet the surface, a thin layer of air exists between solid and liquid. This also displaces liquid, making the apparent volume of the material larger. In tests like ASTM D 2965, where the volume of paint film being tested is very low, this error can be significant. Materials called surfactants can be added to increase wetting, but they affect the density of the liquid. Where surfactants cannot be used, another liquid must be used.

Permeation—When the liquid meets or wets the surface with total penetration into the bulk of the material, the volume of liquid displaced is equal to the skeletal volume of the material being tested. If there are small molecular weight molecules left inside the bulk of the solid, these can migrate out, leaving the testing liquid in its place. These will change the bulk testing liquid's density as they accumulate.

MEASUREMENT SYSTEM UNITS, CONVERSIONS, DENSITY, AND RELATIVE DENSITY

Today's world uses three systems of measurement [*4*].

1. International System of Units (SI), previously referred to as the metric system, based upon powers of ten. This was called the MKS system, standing for meters (distance), kilograms (force), and seconds (time). A common form of this system uses millimetres, grams, and seconds as the units. By universally accepted definition, 1.0000 g of distilled water occupies 1.0000 cm^3 (or 1.0000 mL) at 4.00°C.
2. The British system uses the British yard (distance), pound (force), and second (time).
3. The United States (U.S.) system uses the U.S. yard (distance), pound (force), and second (time).

The British and U.S. systems use the same basic linear distance and force units, but, when measuring volumes, the systems do not have equivalency. A British gallon of water (volume) weighs 9.993 lb at 77°F (25°C), while a U.S. gallon of water weighs 8.321 lb at 77°F (25°C) [*7*].

Conversion between the three systems can be accomplished using the following relationships:

$$\begin{aligned} 2.54\ \text{cm} &= 1.00\ \text{in.} \\ 231\ \text{in.}^3 &= 1.00\ \text{U.S./gal} \\ 453.6\ \text{g} &= 1.00\ \text{lb} \\ &\text{or} \\ 277.4\ \text{in.}^3 &= 1.00\ \text{British (Imperial) gallon} \end{aligned}$$

From SI to U.S.:

$$(2.54\ \text{cm/in.})^3(231\ \text{in.}^3/\text{U.S. gal})/453.6\ \text{g/lb} = 8.345\ \text{cm}^3\cdot\text{lb/U.S. gal}\cdot\text{g} \quad (11)$$

$$(2.54\ \text{cm/in.})^3(277.4\ \text{in.}^3/\text{British gal})/453.6\ \text{g/lb} = 10.02\ \text{cm}^3\cdot\text{lb/British gal}\cdot\text{g} \quad (12)$$

These are conversion factors, which carry particular units. They are used to convert density values for a material at any temperature into a second set of units at that same temperature. The 8.345 factor for conversion to U.S. pounds per gallon is sometimes confused with the 8.320 value for a U.S. gallon of water at 25°C (77°F) [*2*].

Density (in the SI system) at any temperature = density (in the U.S. system) × 8.345 at the same temperature.

Example for pure water at $°C (39.2°F):

$$\frac{1.000\ \text{g}}{1.000\ \text{cm}^3}(\text{SI}) = 1.000 \times 8.345\ (\text{conversion}) = 8.345\frac{\text{lb}}{\text{U.S. gallon}}\ \text{at 4°C}$$

for pure water at 25°C (77°F):

$$\frac{0.997\ 04\ \text{g}}{1.000\ \text{cm}^3}(\text{SI}) = 0.997\ 04 \times 8.345\ (\text{conversion}) = 8.321\frac{\text{lb}}{\text{U.S. gallon}}\ \text{at 25°C}$$

Note in these examples that the volume of space (container internal volume) has not changed with temperature. But, the amount of material which can fit into that volume has

changed with temperature! Using known volume devices provides *only* density values. Temperature must be stated as a significant variable.

LIQUIDS

Densities of Liquids—Methods of Determination

Buoyancy-Hydrometers

Hydrometers are flotation devices that are calibrated using water at various temperatures. When placed in clear liquids, the relative density is read directly from the scale on the hydrometer. The hydrometers range from low-cost, low-precision, to expensive, high-precision devices. Better-grade hydrometers also have incorporated thermometers for temperature corrections and greater independence of reading liquids in an as-is condition. A balance or a known volume device is not needed with this technique. Simplicity is the advantage of this technique. Shown in Figs. 12 and 13 are two types of hydrometers. The catalog text has been included to explain ranges and features unique to these devices.

ASTM methods using hydrometers are [*9,10*]

Test Method for Apparent Density of Industrial Aromatic Hydrocarbons (D 2935)

Test Method for Calculation of Volume and Weight of Industrial Aromatic Hydrocarbons (D 1555)

Displacement—Submersion—Specific Gravity Balances

A specific gravity balance is similar to the hydrometer. It is actually a balance which measures the counter weight applied to balance a plummet submerged in the liquid sample. The weight and volume of a mercury-filled elongated glass bulb (plummet) is determined by comparison with standards established by regulatory agencies and traceable back to well-characterized standards, referred to as primary standards, established by national scientific bureaus. The plummet is attached to a balance and submerged into a liquid to displace some of the liquid's volume. The change in weight is attributed to the weight of the displaced liquid. The plummet's volume is known, and it is related to displacement of water. These are related back to water as a calibration liquid, so they provide a relative density rather than a true density. With this device, the sample does not need to be clear because there are no markings on the plummet. The devices also allow the liquid to be at temperatures other than 4.0°C. This type of device is good for solvents and low-volatility materials. Two balances are shown in Fig. 14 and are from recent scientific lab supplier catalogs [*11*]. The catalog descriptions have been included because they are concise statements about the devices, their operating principles, ranges, and other relevant information.

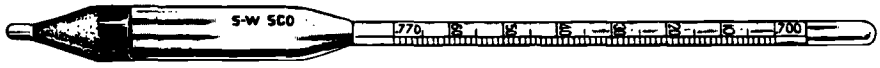
ASTM method using submersion:

Test Method for Specific Gravity (Relative Density) and Density of Plastics by Displacement (D 792)

Displacement—Fluid External Media

This is a device where the sample-holding chamber is not of a known, calibrated volume. A helium gas pycnometer can be used to determine the volume of a liquid in a metal or glass container. The pycnometer's test chamber volume is first established by determination of gas pressure differences in a sample chamber and after expansion into a connecting expansion chamber. Then an independent, empty sample container is introduced into the gas pycnometer test chamber and tested. The reduction in volume is allocated to the empty sample container. The independent sample container's weight is measured on an analytical balance. The sample is added to the sample container and weighed. The container and sample are tested again to establish a new volume.

The sample volume is (sample + container volume) − container volume. The sample weight is (sample + container weight) − container weight. Density is (sample weight/sample volume). The test is fairly fast. Containers of predeter-



Precision Hydrometers for Light and Heavy Liquids—175 mm

A series of short range hydrometers with an accuracy of 0.001, calibrated 60° /60°F. Design corresponds with ASTM specification E100 for plain hydrometers. With smooth, easily cleaned shapes, solid metal ballist, and cemented paper scales. Subdivisions, 0.001.

Cat. No.	Range		
S41885-F	1.000	to	1.070
S41885-G	1.060	to	1.130
S41885-H	1.120	to	1.190
S41885-I	1.180	to	1.250
S41885-K	1.240	to	1.310
S41885-L	1.300	to	1.370
S41885-M	1.360	to	1.430

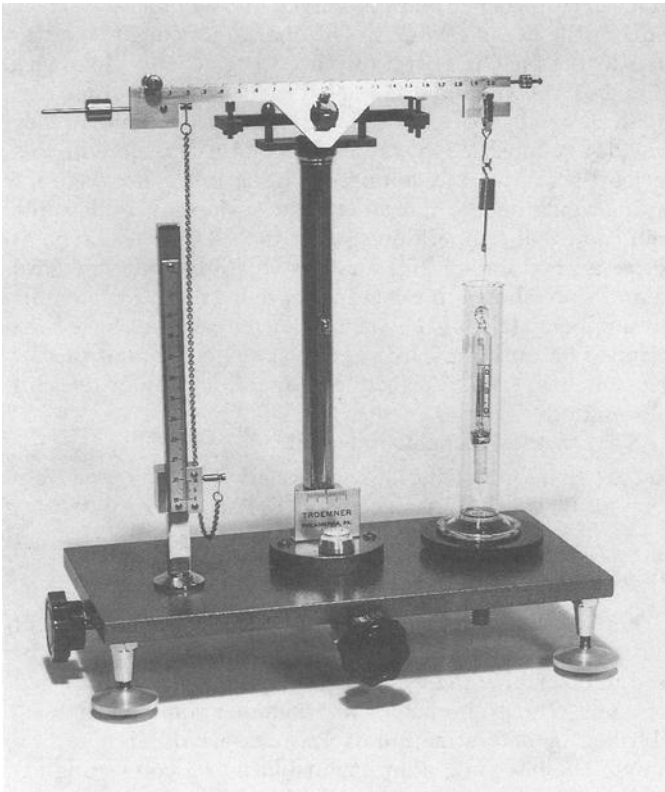
FIG. 12–Hydrometers—specific gravity scale—plain design [*6*].

Sugar Hydrometers with Brix Scale and Enclosed Thermometers—380 mm

Hydrometers are similar to S42436, but provided with a thermometer, range 0° to 50°C in 1° subdivisions, and with scale of correction values in red.

Cat. No.	Range
S42440-B	0 to 12
S42440-C	9 to 21

FIG. 13–Hydrometer—sugar with Brix scale and enclosed thermometer [*6*].



Chain Balance

For liquid densities from 0.0001 to 2.110

Chain gravitometer balance determines specific gravity of liquid with high degree of accuracy. Uses both plummet displacement principle and chain weight system for weighings. No calculations or riders are needed.

Instrument is prebalanced at zero reading by adjusting counterbalance weights. Plummet is immersed in liquid sample. Balance is zeroed again. Single roller-type weight is moved to notch on beam where equilibrium is approached; final adjustment is accomplished by raising or lowering one end of rhodium-plated bronze chain. Specific gravity is determined by adding rider and chain-support readings.

FIG. 14–Specific gravity balances—chain balance and Mohr Westphal balance with catalog text instruction and comments [*11*]. (Courtesy of Fisher Scientific)

mined volume can be kept available to help shorten testing time. Precision and accuracy are good. No ASTM test exists as yet for this technique [*12*].

Displacement—Known Volume Devices—Fluid Internal Media

These are devices of known, internal volume. They have many names such as liquid pycnometers, U.S. standard weight per gallon cups, U.S. mini weight per gallon cups, British standard weight per gallon cups, "featherweight" type weight cups, and Monk cup [*7,13*]. Liquid pycnometers come in a variety of sizes, shapes, volumes, and materials of construction. For precision, glass (inert, light weight, and transparent) is usually used. For testing demanding repeated use, other materials with reasonable inertness or resistance to chemical attack, such as stainless steel, are used. To combine both the light weight of glass and the ruggedness of metal, a "featherweight" construction of anodized, high-tensile aircraft alloy is employed at a cost consistent with the use of specialized materials of construction. The Monk cup is a special design (Fig. 15) and discussed under the topic of handling entrapped air in samples.

Liquid pycnometers or gallon weight cup vessels are built with a main body or container volume, a cap or lid with a vent hole, and sometimes a tare weight object. The tare weight is used as a counter weight for dual pan balances. The weight read after correcting for the tare weight is attributed to the material contained in the vessel at a level which reaches the top of the vent hole in the cap (see Fig. 16).

Both the vessel and a sample of the material to be tested are equilibrated to room temperature or a constant temperature bath temperature by immersion in the bath. Common temperatures for paint and solvent testing are 20°C (68°F) and 25°C (77°F) because these are temperatures in the human comfort range. Temperatures greater than these would drive off solvents. Moisture is not likely to condense out on surfaces from being too cool (weight gain drift during weighing), and volatile materials will not evaporate at a rate that significantly affects the weight readings taken (weight loss drift during weighing). Temperatures colder than these are easily obtained, but are less comfortable for the tester. However, any temperature can be used if the temperature is noted and the vessel volume is corrected for that temperature. If the bath is used, the vessel exterior must be dried off. This has to be done with minimum handling to prevent temperature changes from heat exchange by hands or drying materials.

Next, a portion of the tempered sample is poured into the vessel up to the top rim. The lid is carefully placed on the vessel so that the excess liquid is forced up through the vent hole in the lid *without* coming out around the lid lip. The excess is carefully cleaned off the surface of the lid and from around the lid lip. This is a cleaning, not merely a wiping off. Wiping leaves residues, which affect the results obtained. The sample-containing vessel is then carefully weighed.

Afterwards, the vessel and lid are cleaned as soon as possible and as well as possible to prevent buildup of residues, which will change the vessel's volume. A verification should be performed at frequent intervals with distilled water to catch inaccuracies from poor cleaning or damage to the vessel surfaces. For improved accuracy, the vessel can be calibrated using pure water at normal reading temperatures. Divide the gram weight of distilled water by the weight determined by direct testing. This produces a correction factor. This factor number is multiplied by the weight of the gallon weight found for an unknown liquid or mixture. If the determined density of water was less than expected, a factor greater than 1.000 is generated. As a result, the vessel's volume is less than expected. Tracking the factor value will alert the tester to problems arising from poor cleaning or rough handling that can damage and alter the testing vessel.

Sample sizes range from 10 to 84 mL. The combined weight of the vessel, lid, and sample affect the type of balance which can be used to provide good repeatability and reproducibility. The larger the size, the easier to get a sample representative of the bulk material. But the larger the size, the harder to remove entrapped air bubbles from the sample introduced during sample collection or preparation. For very

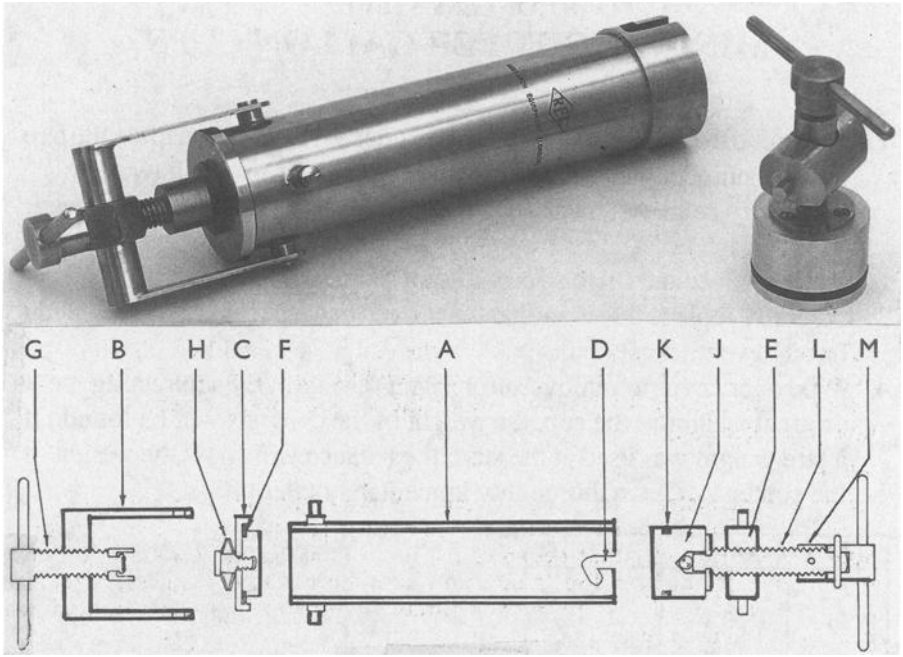


FIG. 15–Monk cup (weight per gallon cup) (courtesy of C. J. Monk and Journal of Oil and Color Chemists' Association) [2]. See Ref 2 for a discussion of Parts A to M.

volatile solvents, use of larger size vessels offsets the weight drift seen during weighing.

The problem of entrapped air can be countered in two ways:

1. The Monk cup is designed to pressurize the sample to 150 lb/in.^{2} in a known volume of space. This pressure compresses the entrapped air in the sample to such an extent that occluded air bubbles are reduced to a negligible volume. Entrapped air of up to 10 vol% can be dealt with by this technique. The volume produced is still larger than the true volume, and a density error is still present. Entrapped air should not be accounted for if the air escapes before use or the air is an artifact of sample mixing before testing. The Monk cup is large and heavy and requires use of nonanalytical balances [2]. Figure 15 is a schematic diagram and picture of a Monk pressure weight-per-gallon cup.
2. An alternative technique is to mix a measured weight of the unknown density material with the weight of a known diluent from a full weight per gallon cup. The blend is then placed back into the cup and then weighed. The following, enclosed in quotes, is copied directly from the GARDCO minicatalog Number 9, including the diagrams, with permission from GARDCO [7].

$$X = \frac{W_{\text{unknown}} B_{\text{lend wt per gallon}}}{(W_{\text{unknown}} + W_{\text{diluent cup weight}} - 10\, B_{\text{lend wt per gallon}})} = \frac{WB}{(W + A - 10B)} \quad (13)$$

where $A = W_{\text{diluent cup weight}}$

"Heavy-bodied materials which entrap air present a problem in true weight per gallon (density) measurements. Air entrapment causes the apparent volume of a material to be greater than actual and density or weight per gallon calculations are low and erroneous. The practice of measurement under pressure does reduce the error but the error is far from eliminated as the entrapped air is normally not removed, but only compressed as shown in Figs. 17 and 18."

"Most materials that are difficult to evaluate can be simply and accurately measured by the following depicted procedure."

"A measured weight of the unknown material is thoroughly blended with the weight of a known diluent from a full weight per gallon cup. The blend is then placed in the cup and the weight per gallon is determined. The value of the unknown material is calculated from the formula given above. The diluent liquid must be compatible with the material containing the entrapped air and it must be thin enough in viscosity to allow entrapped air to rise to the blend's surface and escape. In the case of particulate, such as pigment, the liquid must be able to wet the particle surfaces and displace air in pockets or depressions on the surface."

ASTM methods using known volume devices are [*13,14*]:

Test Method for Density or Relative Density of Pure Liquid Chemicals (D 3505)

Test Method for Density of Paint, Varnish, Lacquer, and Related Products (D 1475)

Sonic Frequency Shifts

Waves of air reaching a human ear are recognized as sound. The pitch of a sound is related to how many waves reach our ear per unit of time. This unit of time is referred to as *frequency*. Waves are made by an object moving in the media: air or liquids or even solids. The media touched by the wave can pass this movement through itself. When a boundary between two media of different densities is encountered by the wave, two actions occur: (1) some waves are reflected back; (2) a portion of the waves are passed into the new media but with their frequency changed.

STAINLESS STEEL

MINI WEIGHT PER GALLON CUPS

METHOD OF USE

1. Determine the weight of a clean cup in grams. As an alternative, the cup may be supplied with an accurate tare weight for use with two-pan laboratory balances. Note: Do not interchange tare weights between cups as each cup and tare weight is matched.
2. Remove cover and fill to within 1.7mm of rim with material to be tested.
3. Carefully replace cover so that the air and excess material is expelled through vent.
4. Wipe over cover to remove surplus and reweigh. By subtracting the original weight of the cup, the weight of the contents will be found. If a tare weight was used at the start, the balance will show the weight of the contents. Clean thoroughly immediately after use.

TEMPERATURE		WEIGHT
C.	F.	Grams
21	69.8	8.329
22	71.6	8.327
23	73.4	8.325
24	75.2	8.323
25	77.0	8.321
26	78.8	8.319
27	80.6	8.316

DETERMINING ACCURATE CUP FACTOR

Comparative results on different materials measured in the same cup are accurate to within the limits of sensitivity of the balances used. Comparative results between cups may be improved by determining a cup factor as follows: Divide 99.925 by the gram weight of distilled water held by the cup at 25°C to determine the cup factor. For example, if the weight of water held by the cup is 99.800 grams, divide 99.925 by 99.800 which is 1.0013. Multiply all cup readings by this factor. In the same manner, if the cup holds 100.200 grams, divide 99.925 by 100.200 which is 0.9973 and all cup readings should be multiplied by this factor.

FIG. 16–Mini-weight per gallon cups [7].

Changes in density also lead to changes in frequency. This can be demonstrated by filling a matched set of water glasses to different levels with water, then striking each glass lightly to produce a sound. The higher the water level, the higher the tone. Just as the frequency changes from an empty glass (air, less dense) to a high frequency tone when filled with water (more dense), the replacement of liquids of differing densities also shifts the frequency for glasses filled to the same level. This is the principle for several digital density meters commercially available today.

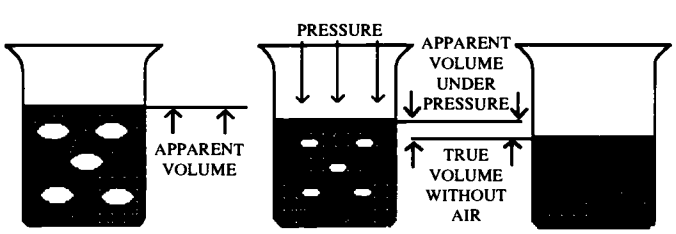


FIG. 17–Liquid with entrapped air [7]. Figure provided by Paul N. Gardner Co., Inc.

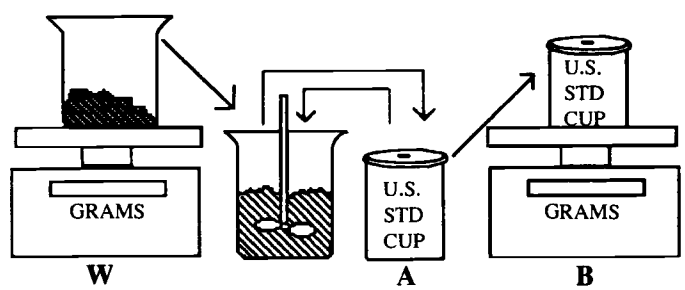


FIG. 18–Diagram for mixing known and unknown density materials [7]. Figure provided by Paul N. Gardner Co., Inc.

Measuring devices have been devised using a glass tube, an oscillator, and a sensor. The oscillating frequency of the tube changes when air is replaced with a liquid. The instrument can use air and water to establish a set of constants, called A and B, for the following relationships [15]

$$A = (T_w^2 - T_a^2) \div (d_w - d_a) \tag{14}$$

$$B = T_a^2 - (A \cdot d_a) \tag{15}$$

where

T_w = observed period of oscillation for cell containing water,
T_a = observed period of oscillation for cell containing air,
d_w = density of water at test temperature,
d_a = density of air at test temperature,
t = test temperature expressed in degrees Kelvin,
p = test barometric pressure expressed in torr,
d_a (g/mL) = $0.001\,293 \times (273 \div t) \times (p \div 760)$
d_w (g/mL) = 0.997 04 at 25°C (273 + 25 = 298°K)

Constant A is used by the instrument's computer to calculate constants K_c and K_{cr}. Constant B is used by the instrument's computer to return the reading for air density.

Modern digital density instruments are equipped with heating and cooling devices internal to the instrument, such that the sample can be equilibrated within the instrument in a matter of seconds. This leaves the pressure term, P, as a visible variable. Pressure changes can occur over a period of time due to weather changes.

The sample tube must be cleaned after each use. The tube's condition needs monitoring to verify that it is at original condition. Frequent calculation of the instrument cell constant K_c overcomes both of these problems.

For density values

$$K_c = \frac{1}{A} = \frac{d_w - d_a}{T_w^2 - T_a^2} \tag{16}$$

$$d_{\text{material}} = d_w + K_c \cdot (T_a^2 - T_w^2) \tag{17}$$

For relative density values

$$K_{cr} = \frac{1.0000 - d_a}{T_w^2 - T_a^2} \tag{18}$$

$$d_{\text{material}} = 1.0000 + K_{cr} \cdot (T_s^2 - T_w^2) \tag{19}$$

where

T_w = observed period of oscillation for cell containing water,
T_s = observed period of oscillation for cell containing sample,
K_c = instrument constant for density,
K_{cr} = instrument constant for density,
d_w (g/mL) = 0.997 04 at 25°C (273 + 25 = 298 K) density of water at test temperature, and
t = test temperature expressed in degrees Kelvin.

Small process computer chips built into commercially available instruments handle all the necessary calculations. Small sample volumes (1.0 to 2.0 mL) are used so heterogeneous samples like paint must be well mixed. The samples must be free of entrapped air. Small amounts of air cause fluctuations in the readings. Use of dilution with a compatible solvent (of known density) to thin the sample can be used if the thinning does not cause pigment dropout. The contribution of the thinner solvent can be calculated and backed out.

The ASTM method using the digital density meter is [*15*]:

Test Method for Density and Relative Density of Liquids By Digital Density Meter (D 4052)

SOLIDS

Densities of Solids—Methods of Determination

With solids, determining the volume for a known weight of the material is a challenge for several reasons. First, the form is fixed and direct, accurately known volumes are the exception rather than the rule. Second, solids are seldom homogeneous in their density. Processing often introduces voids or regions of differing degrees of crystallinity, both of which effect density. For large objects, displacement techniques as well as sonic shifts are useful. For powders and small particles, displacement and density by mixing with liquid diluent are the most common techniques. For thin films, only displacement techniques are useful.

Direct Volume Measurement by Pycnometer

Pigments are insoluble, solid particles used to impart color or light reflectance in paints. To provide more than an apparent density, special steps must be taken. ASTM Method for Specific Gravity of Pigments (D 153) is a set of three variations on the diluent pycnometer technique described in Fig. 18. It uses a vacuum pump and vacuum desiccator or bell jar to reduce the pressure on a sample of solid pigment. Variation A places a weighed sample of pigment in a dry, weighed glass pycnometer. White kerosene is then added to cover the pigment. The pycnometer and sample is then placed in the dessicator or bell jar and slowly evacuated to remove air entrapped on the irregular surfaces of the pigment. This is a method to wet the pigment surface and remove the contribution of entrapped air in the pigment. After all bubbling stops, air is let back into the jar and the pycnometer is filled to the top with kerosene and weighed. Variation B evacuates the pycnometer before the kerosene is added. Most of the kerosene is added to the pycnometer while it is under vacuum. The pycnometer is topped off with kerosene after returning to normal pressure. Variation C uses a measuring burette to add the kerosene so that volume of kerosene added is known [*2*].

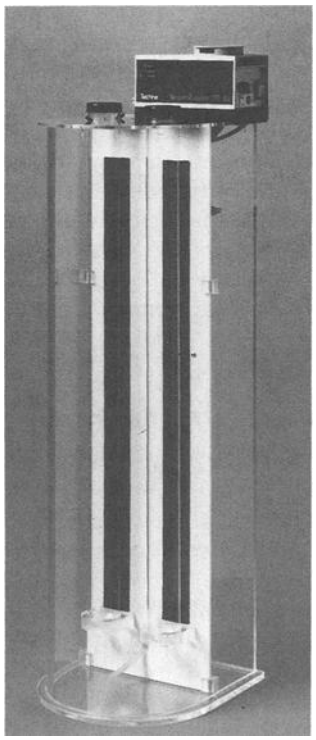
ASTM methods using pycnometer are [*2,16*]:

Test Methods for Specific Gravity of Pigments (D 153)
Test Method for Density (Specific Gravity) of Solid Pitch (D 2320)

Displacement of Liquids

This was discussed in the section on Solids, Liquids, and Gases as concepts and under ideal conditions.

Density gradient column systems (Fig. 19) are another form of submersion test methodology, inverted from the plummets of the density balances. Here the fluid is the calibrated, known test media, and the solid is the unknown. A vertical column tank with black background is carefully filled with a mixture of liquids in a very strict order to establish a heavy-to-light liquid density gradient. Measurements are made by adding in both unknown solid materials such as fibers, film pieces, powders, and glass particles and reference materials of known density. The particles will sink to the level of their own density. Using the proper reference materials, exact matches can be established within 0.0001 g/mL. There is a problem when the sample interacts with the fluids and



For accurate density determination of small solid samples to 0.001g/mL. Conform to ASTM D1505-68 for testing plastics. Measurements are made with reference to standard glass floats calibrated within ±0.0001g/mL. Fibers, irregular fragments, pieces of film, powders and glass are suitable. Several determinations can be made at same time.

In wide use for testing polyolefins, fluorocarbon polymers, nylons, PVC. Can separate natural and synthetic fibers. Can assay factors affecting density such as degree of crystallinity of plastics, concentration of isotopic content, presence of trace amounts of boron in silicon.

FIG. 19–Density gradient column systems with text from supplier catalog [*6*]. (Courtesy of Fisher Scientific)

absorbs them or interacts in other chemical ways which perturb the normal test action as with inert materials such as glass or plastics. Powders with irregular surfaces can also experience surface wetting problems and air pocket entrapment. Densities can be determined from 0.79 to 2.89 g/mL with this technique [*24*].

The test is of long duration, requiring a settling time of usually several hours. Several caution notes are included concerning thin film samples and their handling which could change the density. Potential users should review ASTM D 1505 to assess the applicability of this technique to their own personal needs and use.

ASTM methods using displacement of liquid and gases are [*17–19*]:

Standard Test Method for Volume Nonvolatile Matter in Clear or Pigmented Coatings (D 2697)

Test for Specific Gravity (Relative Density) and Density of Plastics by Displacement (D 792)

Standard Test Method for Density of Plastics by the Density-Gradient Technique (D 1505)

Displacement—Gases

Helium pycnometers have been available for a number of years with many people expressing interest in using these devices to determine the volume of solids of known weight. These instruments are usually relatively expensive and only recently have become sufficiently automated to reduce the intense manual labor required to do a good job. Test method activities are being pursued with ASTM paint committee D 01.21 for thin film (ASTM D 2697) volume solids [*1,12*]. The main problem is to provide a sufficient amount of free paint film to test at a valid film thickness. Films that are too thick can retain solvents. Films that are too thin are very hard to handle. Free films develop static charge buildups which further complicate the testing procedure.

Dry powders are a second candidate for this technique. Helium gas displacement eliminates the need for the vacuum pump and the kerosene used in ASTM Method D 153, Test Methods for Specific Gravity of Pigments, to replace the air in the voids and available surface cavities. The drawback is that the fine powder is easily blown around. The instrument must be designed to eliminate powder travel and to keep the fine particles from the valves and seals. Helium pycnometery may become the method of choice as methods are developed and exchanged in the standard testing methods arena [*2*].

ASTM methods using Helium Pycnometery [*21*]:

Test Method for Density of Solid Pitch (Helium Pycnometer Method) (D 4892)

Sonic Frequency Shifts

The sonic frequency shift, principle and equations, has been discussed previously. Use of the sonic technique is limited to continuous objects which can be cut and shaped. Powders and small particles can be suspended in liquids and tested using the equipment discussed previously and using the equations noted earlier under **Sonic Frequency Shifts.** When the instrument uses solids instead of liquids, several considerations change. A glass tube is no longer used. The solid specimen must be cut into a rectangle with a smooth surface. Surface flaws will introduce errors in the readings.

A sonic sensing head is attached to the solid specimen (approximately 75 mm in thickness), and measures the velocity of sound transmitted through the specimen. Solid specimens require a minimum conditioning time period under controlled temperature and humidity conditions before testing. A calibration curve can be established using materials of known density. The published use is limited to polyethylene plastics. Alternative methods are probably cheaper or less time/labor consuming.

ASTM method using Ultrasound [*20*]:

Standard Method for Density of Polyethylene by The Ultrasound Technique (D 4883)

Apparent Density

Many pigments or powders are tested without regard to the air entrapment on the particle surfaces or in the voids between where the particles touch. These materials are placed in a graduated transparent container, and a vibrator is touched to the container wall. The particles pack down, and a weight is taken. This is referred to as *apparent density.*

ASTM methods based on apparent density include [*22–24*]:

Test Methods for Methylcellulose (D 1347)

Test Methods for Sodium Carboxy Methylcellulose (D 1439)

Test Methods for Hydroxypropyl Methylcellulose (D 2363)

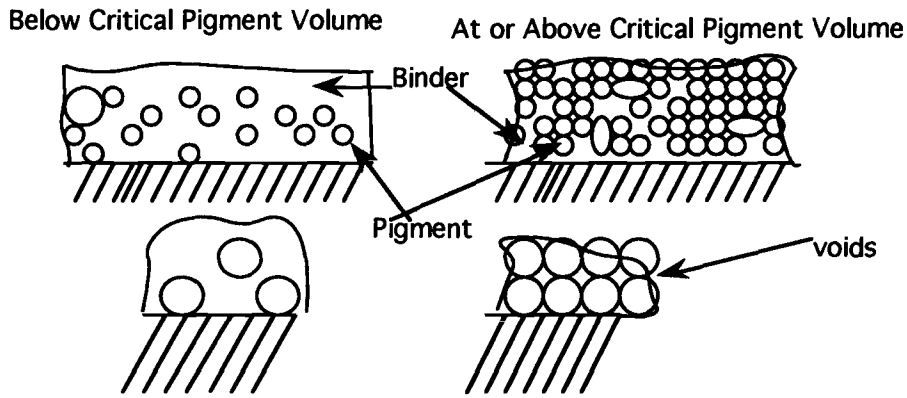


FIG. 20–Pigment volume relationships.

PAINT VOLUME SOLIDS

Paint is a mixture of materials that is designed to protect and beautify a substrate. When paint is sold, it is sold by volume as gallons or liters. What the consumer wants is the most coverage for the money. Commercial painters and original equipment manufacturers paint surfaces to a minimum thickness called "hiding." They know the square footage or square meter surface area they need to cover. With the thickness for hiding known, a volume of solids needed for painting a house or an automobile can be calculated. Government regulators would like to know the volume of volatile organic material included in a gallon of paint. A ratio of volume volatiles to volume solids would be a measure to compare paint products in terms of pollution contribution.

Theoretical Calculations of Paint Volume Solids

For many paint systems in commercial use today, a straight calculation of solids content can be performed with good results using the densities and weight percent content of materials which contribute solids to the final product. For many other systems, however, this calculated answer does not account for additional reaction by-products or provide information about how the density of the material has changed when cross-linking occurs. For these systems an analytically tested answer is needed. The answer would relate to the present U.S. Environmental Protection Agency's (EPA) Reference Method 24: Guidelines of Testing for VOC at 110°C for 1.00 Hour Bake [*1*].

Analytical Determination of Paint Volume Solids

Test Method for Volume Nonvolatile Matter in Clear or Pigmented Coatings (D 2697) is the latest version of this test. The test is based on displacement of liquids, usually water or kerosene. Complications by cured paint surfaces cause this test method to be suspect and is not accepted by EPA for their regulatory purposes. A new method based on volume determination by gas (helium) displacement is under development and evaluation [*1*]. The helium is a pervasive gas that behaves closely to an ideal gas. Where paint surfaces are hard to wet with water, the helium has no problem getting very close to the paint surface and displacing air residing at the surface. The test chambers are usually from 5.0 to 30 cm^3 in volume. The paint sample is introduced as a free film or attached to a carrier such as a metal disk or aluminum foil. When the film is a free film, static charges can build up and cause sample loading and handling problems. The test instrument is not inexpensive, but it is highly automated and minimizes the human labor required to about 5 min per test.

CRITICAL PIGMENT VOLUMES

Definition

A condition when a paint has too much pigment and too little polymer such that internal voids are created which trap air or solvent in the vapor state [*1*].

Effect

A solid is created which has a higher apparent volume than really exists. See Fig. 20.

Relationship to Volume Solids

The present volume solids test uses liquids which are unable to penetrate into the void areas. A larger volume of water will be displaced, and the apparent weight loss will be greater in water. The resin is spread out over the pigment surfaces and will experience less opportunities to cross-link or tangle. The binder will not cure well, and the durability will be poor.

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32

Particle-Size Measurements

by George D. Mills[1]

PARTICLE-SIZE MEASUREMENT ASSOCIATED WITH the paint and coatings industry has broadened in scope considerably over the past few decades. Not only must we evaluate the size, shape, and size distribution of the pigments, fillers, and emulsified resin particles used in the formulation of the coating system, but major efforts are now put forth to address environmental and applicator's health problems that are specific to particle size and nature. Environmental and economic concerns have been a substantial driving force in the development of powder coating technology, which requires monitoring finished powder size and size distribution to ensure consistent application parameters.

We have learned that the size, shape, and nature of dust particles in the air we breathe during the manufacture, application, and abrasive removal of paints are of utmost concern to our health. Airborne dusts of silica, asbestos, as well as lead- and chromium-laden paint debris generated during abrasive blasting are serious health threats. In an effort to protect the general public, government regulations now address the monitoring of small respirable dust particles of less than 10 μm ("R10" particles) during the abrasive removal of certain coatings.

In the production of electronic microcircuits, chips, and semiconductors, photo-resist coatings are applied to silicon wafers with line-to-line resolution of fractions of a micron. Dust particles, which are a fraction of this size, if allowed to contaminate the coated surface, will cause the production of defective chips. Dust has forced the development of more sophisticated clean-room technology in recent years. The reject rate of produced microchips caused by defects in the coating as a result of ultra-small particles of dust is a major problem.

As technology advances in the evaluation of smaller-size particle systems, materials used to standardize and calibrate the measuring/monitoring equipment must be developed. The necessity for standard traceable test materials, i.e., from the National Institute of Standards and Technology (NIST), formerly NBS, which are required to ensure the reliability of the measurements, has led to secondary industries that produce these standards from various materials.

Due to pressing global concerns with solvents emissions as well as the associated economic benefits, powder coatings as a class have grown at a very fast rate over the past 20 years. Many properties impacting the production, delivery, application, and film-forming characteristics are related to the average particle size of the manufactured powder. Often, of equal importance, is the amount of very small particles present. These "fines" affect fluidization and electrostatic application characteristics of the powder. Although an understanding of the relationships of powder properties to product application characteristics and performance is important, quality assurance/quality control (QA/QC) requirements demand high-speed, on-line (real-time) monitoring. This demand for rapid, accurate analysis of particle characteristics has been a driving force in the development of current instrumentation. The availability of low-cost computers and pertinent software as well as highly reliable and stable energy power sources and detectors have allowed the development of fast, accurate, broad spectrum, and "in-process" instrumentation. The development of robust solid-state laser diodes has allowed the replacement of bulky gas lasers, which required optical table stability. Further, the development of fiber optics, as well as the technology associated with its ease of alignment, has assisted in downsizing the footprint of some current generation instrumentation.

A major objective of this chapter is to provide an understanding of the various methodologies available for evaluating particle size, shape, and distribution. The hiding power and light transmission characteristics of coatings are greatly affected by the particle size of included pigments and fillers. Tensile strength of the cured system, water and gas vapor transmission coefficients, chemical resistance, and interface anticorrosive activity are only a few areas impacted by the size, shape, nature, and size distribution of the pigments and fillers formulated into the coating.

This chapter will allow an educated choice of technologies based on the size-dependent measurement most related to the desired property of importance. An appreciation of the mathematics involved will aid in determining and understanding the limitations and potential errors inherent in the measurement.

History of Particle-Size Analysis

The earliest reported particle sizing was about 150 B.C. in Greek and Roman mining manuals using sieves made of leather, woven hair, and planks. The Germans introduced wire-woven screens in the 15th Century. Microscopes were reportedly used in the 1700s for size analysis. Automated machinery was developed in the 1800s for weaving metal-wire sieve fabric. In the late 1800s to early 1900s, standards were developed defining sieve sizes. The first apparatus of record used for classification of pigment particles into different sizes

[1]President, George Mills & Associates International, Inc., P.O. Box 847, Humble, TX 77347-0847.

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was reported by Thompson [*1*] in 1910. Oden proposed the use of gravity sedimentation as early as 1916 [*2,3*].

Energy sources of various wavelengths, employing many different configurations, have been used to measure particle size. Visible light photometry was reported by Stutz and Pfund [*4*] in 1927. Gamble and Barnett [*5*] employed radiation in the near-infrared region. Atherton and Peters reported using light-scattering techniques in 1953 [*6*]. The electron microscope found use in the 1940s for characterizing very small particles as well as to define the corresponding surface topography. The invention of the laser and diode array detectors opened the way for developing the fast light-scattering and blocking instruments widely used in the 1990s.

Importance of Particle-Size Analysis

As the physical properties of paints, coatings, and polymers in general are impacted by the size, shape, and size distribution of the fillers included in the formulation, it is imperative that characterization of the pigment and filler system be correlated with the physical properties of the coating.

Because of the early importance of zinc oxide as a pigment in oil-based paints and its existence in multi forms and shapes, this material was studied in the 1920s and 1930s. Bunce [*7*] found that as the average diameter of zinc oxide in a paint increased from 0.19 to 0.31 μm, the elongation of the film increased and the load at the breaking point decreased (Fig. 1). Eide [*8*] showed that coarse acicular zinc oxide imparted greater durability to a paint than did "round" zinc oxide. In related studies, Morris [*9*] and Nelson [*10*] found evidence that acicular asbestine of a wide distribution of sizes favorably influenced the durability of paints, and a review by Jacobsen [*11*] cites many examples of the significance of particle size and shape of pigments and extenders on the optical and physio-chemical properties of coating systems.

Many surface properties are impacted by the pigment's and filler's particle size and nature of which gloss is one of the most prevalent. While the larger-size particles can "protrude" through the surface of the coating, causing a surface roughness related to the size of included particles, extremely fine particles can affect gloss by adsorbing binder to a point that the gloss is decreased due to a lack of available binder at the coating surface. The "oil adsorption" of the pigment is a function of its surface area and increases as the average particle size decreases. The "critical pigment volume concentration" (CPVC) exists at a pigment loading at which there is insufficient binder solids to completely wet out the included filler and pigment particles. Coatings formulated above the CPVC cannot be glossy. Abrasion resistance of the coating may be increased by the addition of hard fillers such as silica. The relationship between particle dimensions and film properties is depicted in Fig. 2. The National Paint, Varnish, and Lacquer Association has published a Pigment Index that gives information on the particle size of many of the pigments available on the American market [*12*].

Other coating properties impacted by variations in particle size and shape include the efficiency of contained UV blockers and absorbers such as carbon black pigments. The use of acicular pigments such as Wollastonite (asbestos free) are popular in many types of coatings. The tensile and compressive strength of coatings also can be modified by judicial choice of particle size and shape, and gas vapor and molecular water transmission of a coating can be altered with the proper choice of pigment loading and size.

The coalescent and film-forming characteristics of emulsion binders are impacted by the particle size of the dispersed resin particles. Cold touch up, brushability, and mechanical

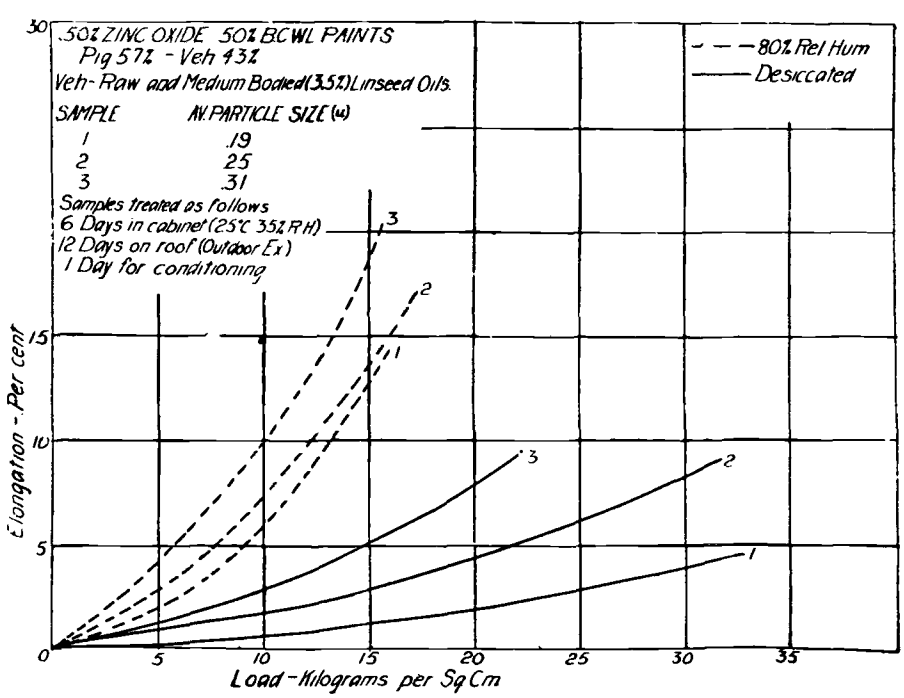


FIG. 1–Stress-strain curves of some paint films. These illustrate the effect of the particle size of zinc oxide on the strength of paint films.

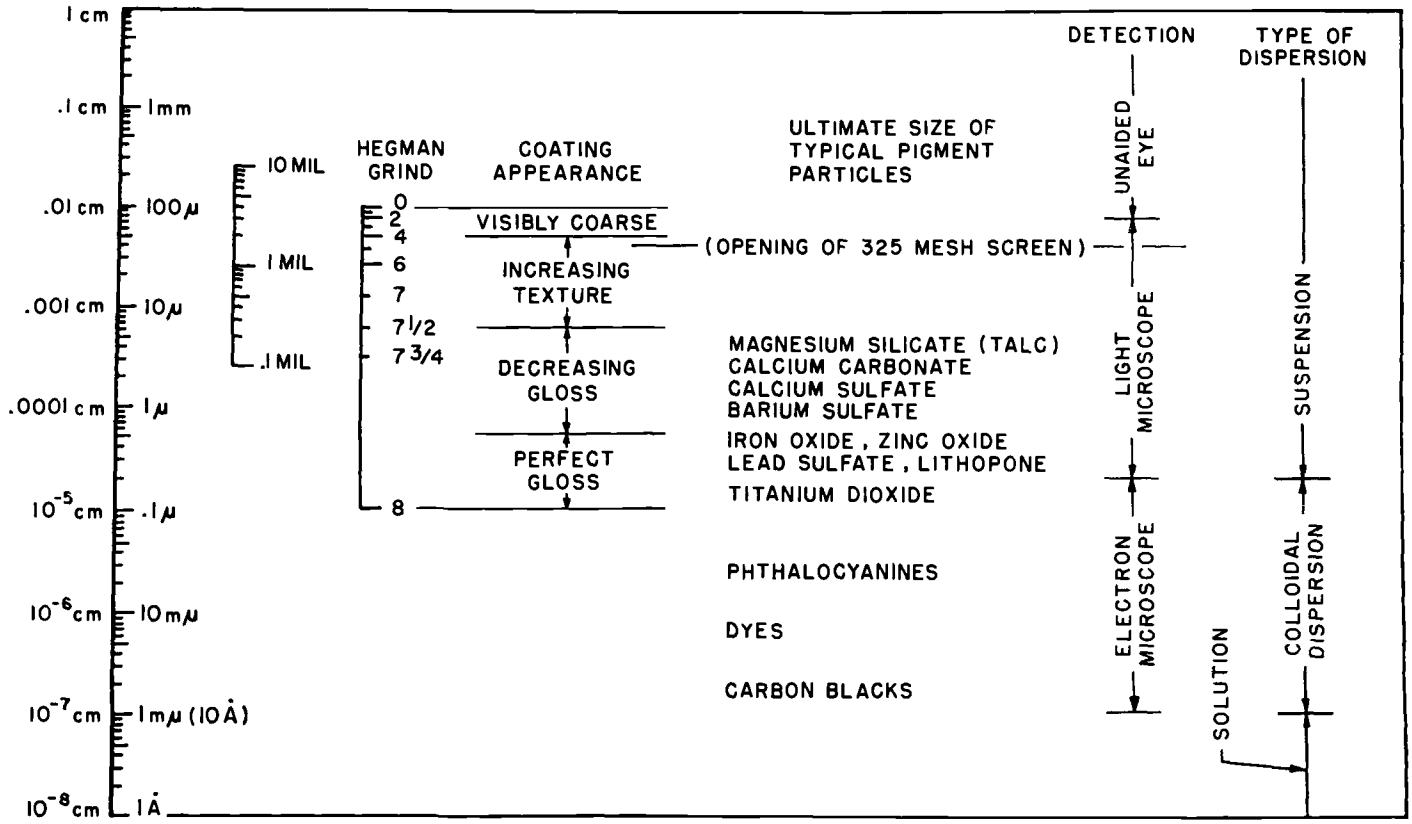


FIG. 2–Dimensions of granular pigments and their relation to surface properties (from Ref *12*). (Courtesy of the *Journal of Paint Technology*.)

stability during pigment dispersion are a function of properties that are related, in part, to polymer particle size. Surfactant demand and effectiveness are a function of polymer particle size (as well as other binder variables). Because of the importance (dependence) of many coating properties on the small finite size of the pigment, fillers, catalysts, and polymers formulated into the coating, the demand for rapid, accurate analysis of particle characteristics has lead to the refinement of many techniques.

CONSIDERATIONS IN SAMPLING TECHNIQUES

Normally, when a particle-size determination is made, one will not work with the total collection of particles comprising the bulk sample. A "representative" collection of particles is usually chosen. This sample is then reduced in size a few more times until only a few milligrams remain for the actual instrumental testing. The assumption is usually made that the fraction actually evaluated is, in fact, "identical" in particle size, size distribution, shape, and nature to the total of the bulk material. This sample test fraction, which usually does not exactly represent the bulk, can be a major source of error, introducing considerable bias and distortion to the results. The reliability of any measurement depends on the degree of representitiveness of the test sample. Thus, the sampling technique is as important (if not more so) than the actual particle-size measurement, though in reality there is little chance that the sample selected will be identical to the bulk material.

Theoretical Considerations of Variance in Sampling

To obtain a representative sample, the sampling process is usually divided into several steps during which a conscious effort is made to reduce bias. The bulk material is usually obtained in huge, ton lots. The first sample reduction provides the "gross" sample, which is on the order of kilograms. This sample is then reduced to the "laboratory" sample, which is on the order of grams. The actual evaluation sample introduced to the instrument is on the order of milligrams. The reduction process will almost always introduce some bias, depending on the actual spread in the distribution. This bias will diminish as the consistency approaches unity, i.e., all particles approach being identical. The bias exists because the physical forces acting on the particles in a collection are not the same, but are, in fact, size dependent. The "fines" act differently in a pile than will the course particles. Their angle of repose is different, often resulting in particle stratification and some segregation.

There are some established rules that must be followed to minimize this bias. The "perfect" sample is one in which the differences seen between the evaluated characteristics and those that actually exist in the bulk can be ascribed to the expected number variations described by statistics. For a sand (A) and sugar (B) mix, the probability that the number fraction, p, of (A) in the bulk actually is represented by the

number fraction (p_i) in the sample is computed from the number of actual particles in the bulk (N) and the reduced sample (n) [13]. The equation is as follow

$$\mathrm{Var}(p_i) = \frac{p(1-p)}{n}\left(1 - \frac{n}{N}\right) \quad (1)$$

Theoretically, the expected deviation (i.e., standard deviation), σ_i, is the square root of the variation. Since the use of the weight fraction is often more convenient, the equation for variance is given by

$$\mathrm{Var}(P_i) = \frac{P(1-P)}{w}[Pw_B + (1-P)w_A]\left(1 - \frac{w}{W}\right) \quad (2)$$

where the weight fraction in the sample and bulk are P_i and P, respectively, W and w are the bulk weight and sample weight, respectively, and w_A and w_B are the weights of individual grains of A and B, respectively.

Even with the "perfect" sample, there is a finite probability that the measured sample will deviate from the actual bulk by some predictable value. To minimize this "guaranteed" deviation, a minimum sample size is required. One may calculate the minimum sample size required to yield values within preset statistical limits [13]. The equation relating the minimum sample weight of a gross sample is given by

$$M_s = \tfrac{1}{2}[\rho/\theta^2][1/w_\lambda - 2]d_\lambda^3 \times 10^3 \quad (3)$$

where

M_s = the limiting weight in grams,
ρ = the powder density in g/cm^3,
θ^2 = the variance of the tolerated sampling error,
w_λ = the fractional mass of the coarsest size class being sampled,
d_λ^3 = the arithmetic mean of the cubes of the extreme diameter in the size class in cm^3.

The collection methods used in obtaining the sample are important. Depending on the nature of the material being tested, samples should be gathered so as to minimize the introduction of bias. There are two "golden rules" of sampling that should be followed when possible [14]. These are:

- The sample should be collected while in motion.
- All of the stream should be collected for a short period of time rather than a portion of the stream for a longer period of time.

This procedure will assist in minimizing the probability of error generated by stratification and segregation due to differing weights of the particles within the stream and of the way they act within the collective mass of the sample during transport. Special collection devices are available for affecting the sample collection.

Sampling Techniques and Equipment

Sampling techniques have been developed to minimize the systematic errors introduced both in collecting the gross sample and in reducing its size to the analytical sample. In the work done by Allen and Khan [15] using sand-sugar and sand-sand, mixtures were evaluated utilizing different collection techniques. These techniques included; (1) cone and quartering; (2) scoop sampling; (3) table sampling; (4) chute riffling; and (5) spinning riffling. The data presented in Table 1 show the values obtained via each method as well as the expected standard deviation from the known sample.

Cone and quartering is a procedure in which the powders are piled into a cone. The cone heap is then carefully pushed down flat and divided into four equal sections. The assumption is that the cone will be symmetrical about its central axis and the flattened sections will all be representative of the bulk mixture. A problem exists as it is very difficult to produce perfect symmetry, which results in some size segregation from the center out. The technique is also operator dependent, and tests showed this technique to give the largest standard deviation of the five techniques evaluated (see Table 1).

Scoop sampling entails randomly dipping into and pulling a scoopful of powder from a pile of the material to be evaluated. Because the pile is usually not totally symmetrical and evenly distributed throughout, the technique is prone to errors. Since in this procedure the powder is not caught while moving, it will not be typical of the bulk lot of material.

Table sampling (Fig. 3) utilizes a tilted surface over which a powder sample is allowed to slide. A series of splitting wedges cut the sample into numerous sections where some portions fall through openings and are discarded. Ultimately, a decreased quantity of sample is collected, although it is necessary that the incoming powder be uniform and consistent.

Chute splitting utilizes a funneling or channeling device capable of alternately placing the powder sampling stream into one of two collection hoppers. The technique is subject to error and operator bias if segregation is allowed to occur in loading the bulk sampling trough. Such error is present when the two collected portions are not the same size.

Spinning rifflers (Fig. 4) utilize a series of smaller collection tubes or holders mounted in a way to collect a flowing powder stream over a very short time period. This technique was found to be the most reliable method for sampling and, when tested with different operators, showed little operator bias. Such was not the case for the other techniques investigated.

PARTICLE CHARACTERIZATION METHODOLOGY

Particles that are perfect spheres can be described by a single value representing the sphere's diameter. Calibrated microscopes are useful in reading such values directly from the reticule. They have some utility with spherical resin parti-

TABLE 1—Standard deviation in particle size determination of a sugar-sand mixture as a function of sampling techniques.

	Standard Deviation (σ)[1]	
	Sugar-Sand	Sand-Sand
Cone and quarter (worst)	5.762	6.812
Scoop sampling	6.312	5.142
Table sampling	2.11%	2.09%
Chute riffler	1.10%	1.01%
Spinning riffler (best)	0.27%	0.132
Random variation	0.09%	0.08%

[1]Binary mixtures of sand-sand and sand-sugar were used, and all particles of one component and none of the other would pass through a designated sieve. Density of sand and sugar, respectively, is 2.65 and 1.64 g/mL. From Allen, T. and Khan, A.A., 1970, *Chemical Engineering*, Vol. 238, pp. 108–112.

FIG. 3–Table sampler: A 16 to 1 reducer with removable legs for portability. (Courtesy of Gilson, Inc.)

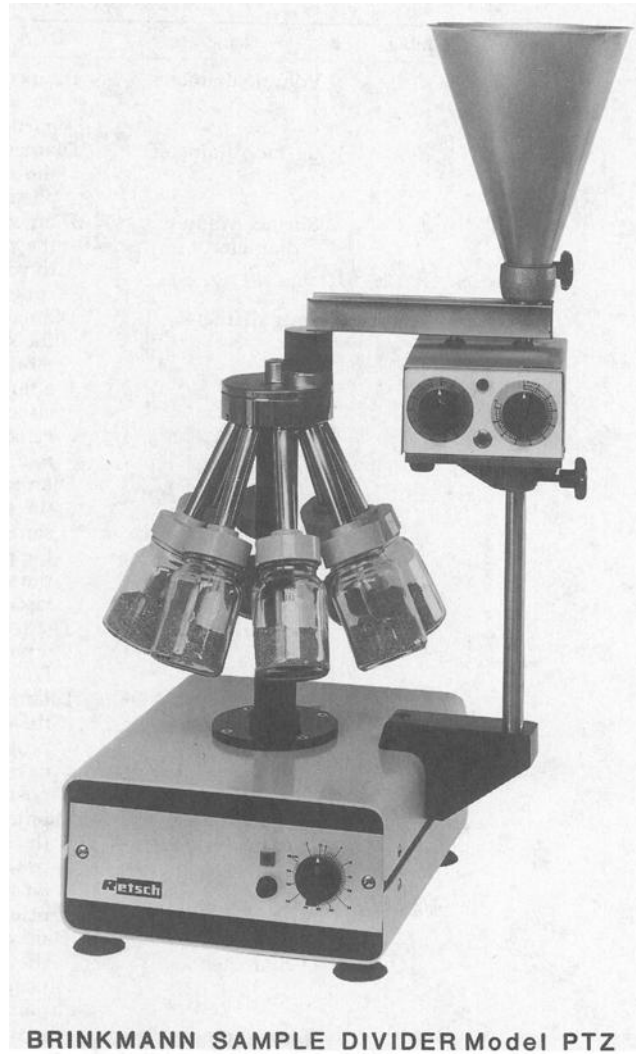


FIG. 4–The spinning riffler. (Courtesy of Brinkman Instruments, Inc.)

cles and with visual measurement of standardized test materials. Classification of most powders, on the other hand, must address particles of various shapes and sizes.

A particle-size determination utilizes some size-dependent property that can be measured and then relates this property to a linear dimension. The measurement derives either from individual particles or as a property of the collection of particles that is often expressed as a diameter of sorts. Measurement of a single individual particle can have many different "diameters" depending on the direction and method of view. Particle characterization, therefore, may involve determining the rate of a particle's travel through a fluid (either under the influence of gravity or while being subjected to angular acceleration due to rotation), its actual surface area, its ability to pass through a screen of square or round holes, or its ability to scatter light of various wavelengths in various directions.

It is convenient to use the term "equivalent diameters" when comparing sizes. The value so determined for a given collection of irregular particles will vary somewhat depending on the technique used (i.e., the size-dependent variable being measured). The definition of some of these "diameters" are presented in Table 2 along with their mathematical representation. Table 3 lists some of the methods, the nominal particle-size range, and the size measured. The methods available for determining particle size take advantage of many different characteristics of the powder particle.

Definitions of Particle Size and Shape

Particle shapes are everything but spherical for pigments and fillers, which are produced, essentially, by crushing and shattering. As the sizes get smaller, the actual particle shape plays an increasingly important role in its use in a coating as well as on the physical laws employed for its characterization. From the diagram in Fig. 5, the same particle may be defined in a number of ways [*16*]. Some of these include the following:

Martin's Diameter—the distance between opposite sides of a particle measured on a line bisecting the projected area. To ensure statistical significance, all measurements are made in the same direction regardless of particle orientation.

Feret's Diameter—the distance between parallel tangents on opposite sides of the particle profile. Again, to ensure statistical significance, all measurements are made in the same direction regardless of particle orientation. Note: Both

TABLE 2—Definitions of particle size.

Symbol	Name	Definition	Formula
d_v	Volume diameter	Diameter of a sphere having the same volume as the particle	$V = \frac{\pi}{6} d_v^3$
d_s	Surface diameter	Diameter of a sphere having the same surface as the particle	$S = \pi d_s^2$
d_{sv}	Surface volume diameter	Diameter of a sphere having the same external surface to volume ratio as a sphere	$d_{sv} = \frac{d_v^3}{d_s^2}$
d_d	Drag diameter	Diameter of a sphere having the same resistance to motion as the particle in a fluid of the same viscosity and at the same velocity (d_d approximates to d_s when Re is small)	$F_D = C_D A \rho_f \frac{v^2}{2}$ where $C_D A = f(d_d)$ $F_D = 3\pi d_d \eta v$ $Re < 0.2$
d_f	Free-falling diameter	Diameter of a sphere having the same density and the same free-falling speed as the particle in a fluid of the same density and viscosity	
d_{St}	Stokes' diameter	The free-falling diameter of a particle in the laminar flow region ($Re < 0.2$)	$d_{St}^2 = \frac{d_v^3}{d_d}$
d_a	Projected area diameter	Diameter of a circle having the same area as the projected area of the particle resting in a stable position	$A = \frac{\pi}{4} d_a^2$
d_p	Projected area diameter	Diameter of a circle having the same area as the projected area of the particle in random orientation	Mean value for all possible orientations $d_p = d_s$ for convex particles
d_c	Perimeter diameter	Diameter of a circle having the same perimeter as the projected outline of the particle	
d_A	Sieve diameter	The width of the minimum square aperture through which the particle will pass	
d_F	Feret's diameter	The mean value of the distance between pairs of parallel tangents to the projected outline of the particle	
d_M	Martin's diameter	The mean chord length of the projected outline of the particle	
d_R	Unrolled diameter	The mean chord length through the center of gravity of the particle	$E(d_R) = \frac{1}{\pi} \int_0^{2\pi} d_R d\theta_R$

Martin's and Feret's diameters are generally used for particle-size analysis by optical and electron microscopy.

Equivalent Circle Diameter—the diameter of the circle having an area equal to the projected area of the particle in random orientation. This diameter is usually determined subjectively and measured by ocular micrometers called graticules.

Equivalent Spherical Diameter (E.S.D.): This often affords a more useful measure, particularly where industrial processing is involved. This diameter is determined, in effect, by measuring the behavior of the irregular particle in a certain circumstance and relating that to the behavior of a sphere of otherwise identical properties.

Sedimentation (Stokes') E.S.D.—the diameter of a sphere of the same density as the particle and having the identical free-fall velocity of the particle.

Volume E.S.D.—the diameter of a sphere having the same volume as the particle.

TABLE 3—Comparison of particle-sizing methods.

	Nominal Range, μm	Size Determined
Gas Permeability	0.1–40	Mean
Gas Adsorption	0.005–50	Mean
Brownian Motion	0.01–3	Mean
Sieving		
Dry	>10	Passing through
Wet	2–74	minimum opening
Microscope		
Optical	0.5–500	Martin's, Feret's, or
Electron	0.002–15	equivalent circle diameter
Zone sensing		
Resistivity	0.05–500	Volume or area
Optical	1–500	
Elutriation		
Laminar flow	3–75	Equivalent spherical
Cyclone	8–50	diameter (E.S.D.)
Centrifugal classification	0.5–50	E.S.D.
Mercury intrusion	0.01–200	E.S.D.
Centrifugal sedimentation		E.S.D.
Mass accumulation	0.05–25	
Photo extinction	0.5–100	
X-ray	0.01–5	
Gravity sedimentation		E.S.D.
Pipettes & hydrometers	1–100	
Photo extinction	0.05–100	
X-ray	0.1–130	
Hydrodynamic chromatography		
Packed column	0.03–2	E.S.D.
Capillary column	0.1–60	
Cascade impactor	0.05–30	Aerodynamic diameter

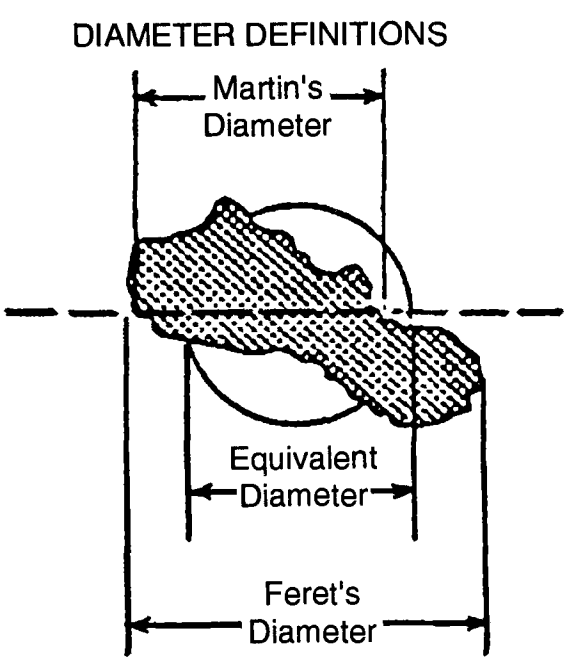


FIG. 5—The relationship of some stated diameters and the physical size of the particle.

Particle Size From Surface Area

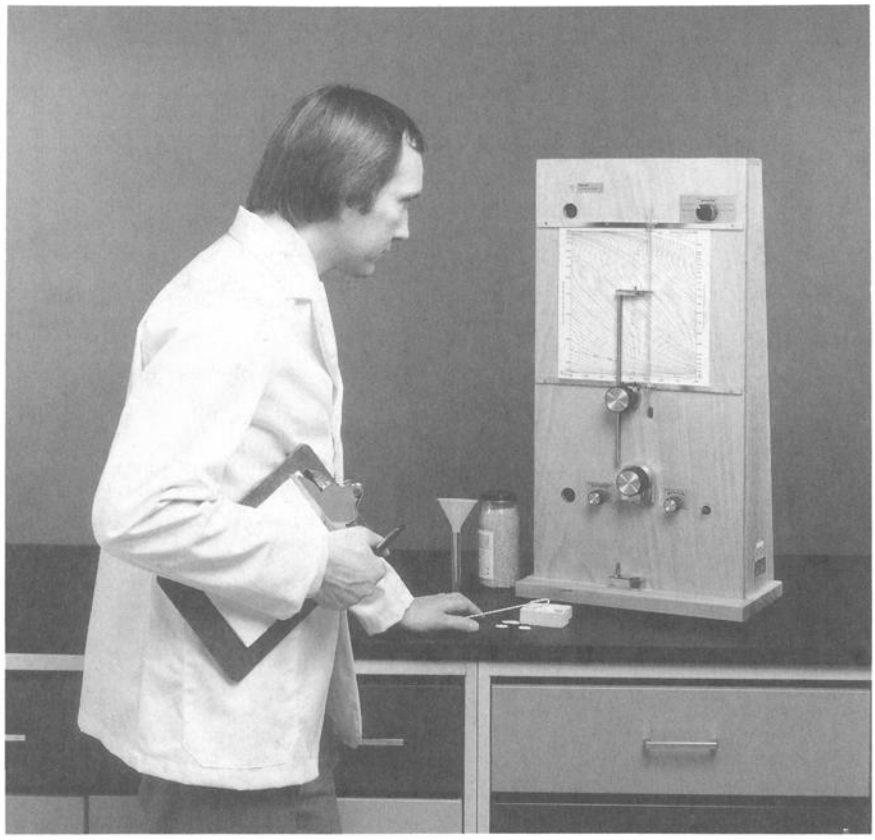
It is often useful to use the approximation of size from surfaces to evaluate other parameters derivable from the volume function, such as specific surface area and density. The basic equations that describe a sphere's surface area and volume are given by

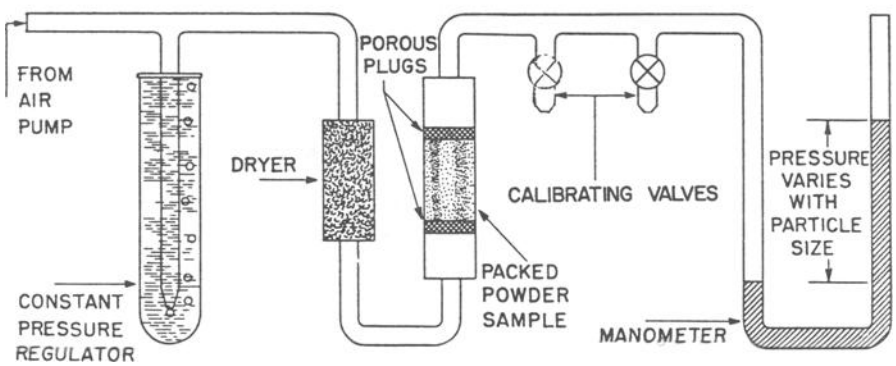
$$\text{Area of a sphere} = \pi D^2 \quad (4)$$

$$\text{Volume of a sphere} = \pi D^3/6 \quad (5)$$

These relationships allow determination of the mean particle diameter if the specific surface (area) is known. Particle-size characterizations that employ surface area techniques in the size determination yield average diameters. The surface area of a powder may be determined from gas adsorption experiments. By assuming uniform-size nonporous and spherical particles, the mean particle size may be determined from the surface area data. The Fisher subsieve sizer is an example of an instrument of this type (Fig. 6). The "specific surface" obtained equals the determined surface area divided by the product of the particle volume and density. With appropriate units conversion,

$$D = 6/[\rho A] \quad (6)$$





1. Perspective of Operating Principles

FIG. 6–The Fisher subsieve sizer. (Compliments of Fisher Scientific.)

where

D = particle diameter, μm,
ρ = particle density, g/cm^3, and
A = specific surface area, m^2/g.

Any shape other than a sphere, either regular or irregular, has a greater ratio of surface to volume, and consequently the particles will be smaller than calculated. Cracks, crevices, and pores are other factors leading to an increase in specific surface area and to a corresponding decrease in calculated particle size.

Perfectly spherical particles are seldom encountered in mineral pigments and fillers used in paint and coating applications since these particles result from shattering by crushers and high-speed pulverizers. Crystalline materials fracture along crystal planes, while some pigments are acicular (like needles). With the many shapes of particles to be evaluated and characterized, instruments that operate on different principles "see" different values of the size-dependent variable being monitored. As a result, a sample characterized by one machine may yield a somewhat different value when

evaluated using a different technique. For this reason, the practitioner must be aware of the size-dependent variable to which his machine is sensitive.

Methods [*17*] for determining specific surface include adsorption of gases by the pigment, adsorption of solutes from solutions by the pigment, and permeability of pressed pigment particles to gases or liquids.

Adsorption of Gases

This method is based on determining the number of gas molecules that will adsorb as a monomolecular layer on the surface of the particles. Knowing the area occupied by one molecule and the number of molecules, the specific surface area of a specimen of pigment may be calculated from

$$\Sigma = nNA \tag{7}$$

where

Σ = specific surface area in cm^2,
n = number of moles of gas per gram of pigment,
N = Avogadro's number, 6.02×10^{23}, and
A = area covered by each molecule.

Knowing the specific surface, the surface mean diameter may be calculated.

Brunauer-Emmett-Teller (BET) Method—The general procedure for this method [*18,19*] includes introducing the specimen into an enclosed space of known volume followed by degassing with heat and evacuation. A known amount of gas is admitted to the system, and its pressure is determined. The gas is then compressed to a new volume, and the corresponding pressure is determined. The procedure is repeated until enough data for the preparation are obtained. By means of the BET equations, the surface area is found, and from it the average particle size may be calculated.

Continuous Flow Method—This method makes use of the BET equation, but the adsorbed gas is determined by concentration measurements in a continuous flow system [*20*]. Nitrogen gas is adsorbed by the specimen at liquid nitrogen temperature from a stream of nitrogen and helium gas and is later eluted by warming the specimen. The amount of nitrogen liberated is estimated by thermal conductivity. For detecting changes in the amount of adsorbed nitrogen, Beresford et al. [*21*] used the Perkin-Elmer-Shell sorptometer with conductivity bridge and potentiometric recorder.

Gravimetric Method—In addition to the volumetric methods, a gravimetric method using balances patterned after that of McBain and Bahr [*22*] can be used. The procedure is much simpler but requires care as the apparatus is very fragile and the changes in weight are very small.

An essential part (Fig. 7) of the gravimetric method is a fused silica spring balance from which a small glass "bucket" for the specimen is hung. The balance assembly is located in a glass housing connected to a source of gas and to a manometer for determining the pressure. The bucket is hung on the balance, the housing is closed, and the specimen is degassed by evacuation. The zero point of the balance is recorded. Gas is admitted to the housing, and the change in weight of the specimen is determined by noting the change in the elongation of the balance with a traveling microscope. Details are set forth in Ref *17*.

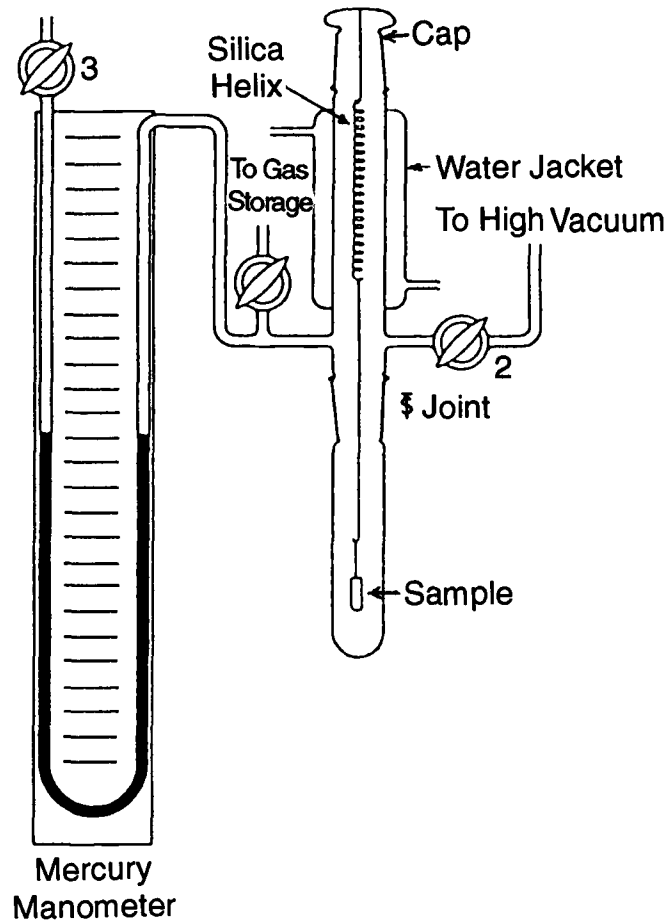


FIG. 7–The Components of a basic gravimetric adsorption apparatus.

Adsorption of Nongaseous Molecules

Adsorption of molecular species other than typical gaseous molecules is possible also. These include the adsorption of solvents and surfactants in special cases.

Adsorption of Solutes onto Pigments—This method depends on the adsorption of solute molecules onto a particle when it is wet out by a solution containing the dissolved surface active solute [*23*]. The process requires that the adsorbent be thermodynamically more active than the solvent and the kinetics be such that wet-out times be reasonable. Typical systems used are stearic acid in benzene, dyes in benzene, and wetting agents in water. The amount adsorbed will asymptotically approach a constant value with time. At this value it is assumed that the surface of the particles is covered with a mono-molecular layer of solute. The area occupied by a single molecule of solute may be obtained from tests made with solids of known areas. The amount adsorbed is obtained by analysis of the solution before and after adsorption.

A disadvantage of the method is uncertainty about the size and orientation of certain types of molecules. On the other hand, the method is rapid and easy to perform. For this reason it is suited to routine tests where its reliability has been established.

Soap Titration of Emulsion Particles—Maron et al. [*24*] determined surface area and particle size of a synthetic latex by

titrating with a soap until the critical micelle concentration of the soap in the solution was attained. From the effective molecular surface area of the adsorbed soap and the amount adsorbed, surface area and particle size are calculated. The method is calibrated with electron micrographs. Brodnyan and Brown [*25*] also studied the technique.

Permeation Through Packed Powders

In this method, a gas, usually air, is forced through a compacted bed of the pigment. The rate of flow is a function of voids (pore space), pressure drop through the bed, specific surface of the pigment, and viscosity of the gas. A knowledge of all the other factors allows calculation of the specific surface area and, from it, the mean surface diameter. The method is fairly simple and is suitable for routine determinations of spherical or near-spherical particles.

Gooden-Smith Method—Using air as the gas, Gooden and Smith [*26*] designed a permeation method with two special features: (1) the weight of specimen used in grams is numerically equal to its density and (2) every specimen is packed to the same volume (Fig. 8). Together with a graphic calculator, these features greatly simplify the test and make it attractive for routine testing or research in the particle-size range 0.2 to 50 μm.

Hutto-Davis Method

The principle differences between this and the preceding method are: (1) the weight of the powder used to make the compacted pellet is calculated to give a definite porosity, and (2) the volume of air is kept constant for all plugs.

Hutto and Davis [*27*] modified the apparatus of Carman and Malherbe [*28*] by providing an improved manometer, better control of the volume of air, and an improved press for preparing the specimen. They also designed a nomograph for calculating specific surface and surface area. The apparatus consists of: (1) a U-tube with legs of unequal length and closed at each end with a sintered glass disk, (2) a manometer, (3) a capillary specimen tube, and (4) a leveling bulb containing mercury.

To provide the constant volume of air, the U-tube is inverted and filled through the stopcock at the bend. Then, with a capillary eyedropper, a weight of mercury equivalent to 1 mL is removed, leaving an equal volume of air after which the stopcock is closed and sealed. The mercury does not pass through the sintered glass disk at the pressure used in the test. To make a test, a plug of pigment is formed inside the specimen tube using the special press. The weight of the specimen is a function of its density and the desired porosity of the plug (usually about 0.5). With the leveling bulb in the lower position, the specimen tube is attached to the side arm of the apparatus, and a vacuum is applied by opening the stopcock at the upper right-hand corner. The vacuum is adjusted, and simultaneously the stopcock is closed, timing is started, and the leveling bulb is raised to its upper position, which forces the 1 mL of air into the system. The timing is stopped when the manometer returns to zero. The stopcock is then opened, and the bulb is returned to its lower position for another run.

Separation and Collection: Particle Size by Elutriation

This approach is primarily a means for separating or fractionating a quantity of pigment into portions according to particle size rather than providing a value of the sizes separated. Size determinations may then be made on the separated fractions. The technique has utility in evaluating the influence of pigment and filler particle size on the properties of the formulated product. After standardizing operating conditions for a material and measuring sizes by an independent method, approximate size distribution may be estimated for additional material.

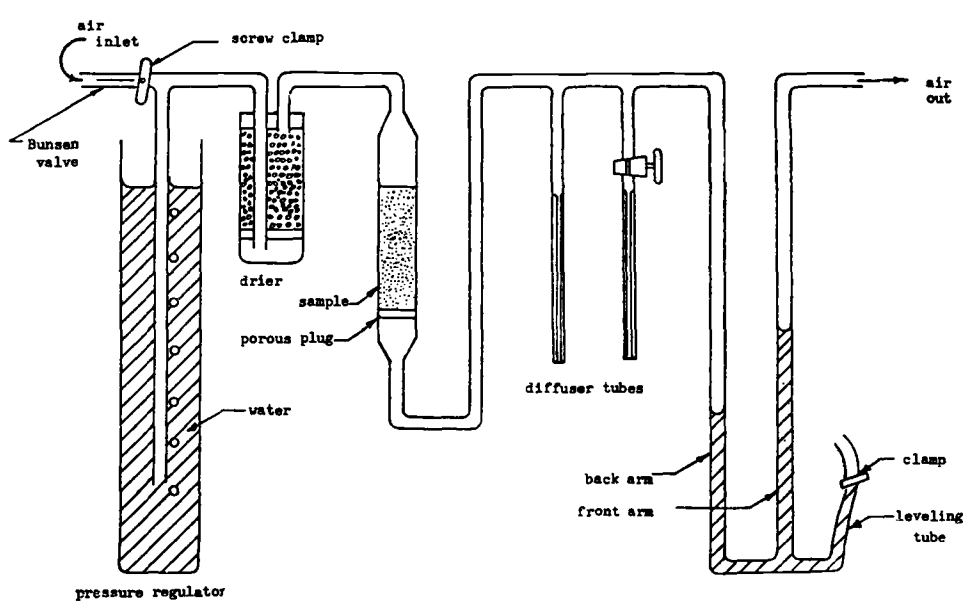


FIG. 8–Gooden-Smith apparatus for surface area. (Courtesy of *Official Digest.*)

Roller Particle-Size Analyzer

This device [*29*] uses elutriation by air to separate pigments into sizes. The glass U-tube at the bottom of Fig. 9 is charged with the specimen of pigment. Air under pressure is admitted through a nozzle that extends to the bottom of the tube. The other arm of the tube is connected to the metal settling tube. By proper selection of size of nozzle, size of settling tube, and velocity of the air, separation into desired fractions is obtained. The fractions are collected in paper extraction thimbles connected with a gooseneck to the settling tube. During the separating, the U-tube and the settling tube are vibrated vigorously. Using 25-g charges, the average time required for separations ranges from 62 min for particles up to 5 μm in diameter to 11 min for particles from 40 to 80 μm in diameter.

Felvation

This method [*30*] combines elutriating and sieving for fractionating fine powders. The basic apparatus (Fig. 10) consists of a column about 4 in. (10 cm) in diameter and 24 in. (61 cm) in height. The specimen is placed in the narrow tube at the right. Fluid is introduced and allowed to pass through at a relatively low rate. The powder soon becomes fluidized in the conical base of the column. The flow of the liquid is increased gradually. The smaller particles reach the sieve and pass through it. The throttling action of the sieve increases the flow through it. Hence, particles that have passed through do not fall back and clog the screen. Eventually, particles just larger than the sieve openings reach the sieve, but they do not block the screen as they reduce the flow around them and then tend to fall from the sieve.

The sieve functions only as a gage. It does not support the powder. Highly accurate electroformed sieves are used, but, because of their small size (1 in. (2.5 cm) in diameter), their cost is reasonable. Beside being economical, the method is rapid. Complete fractionations can be run in a period as short as 10 min.

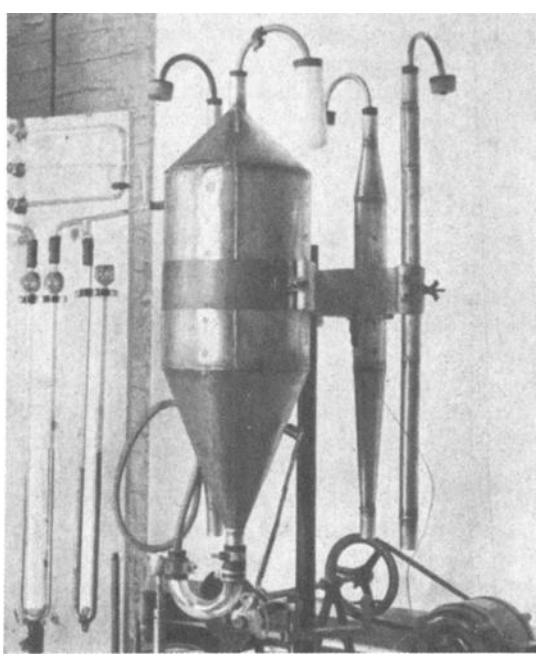


FIG. 9–The roller particle-size analyzer.

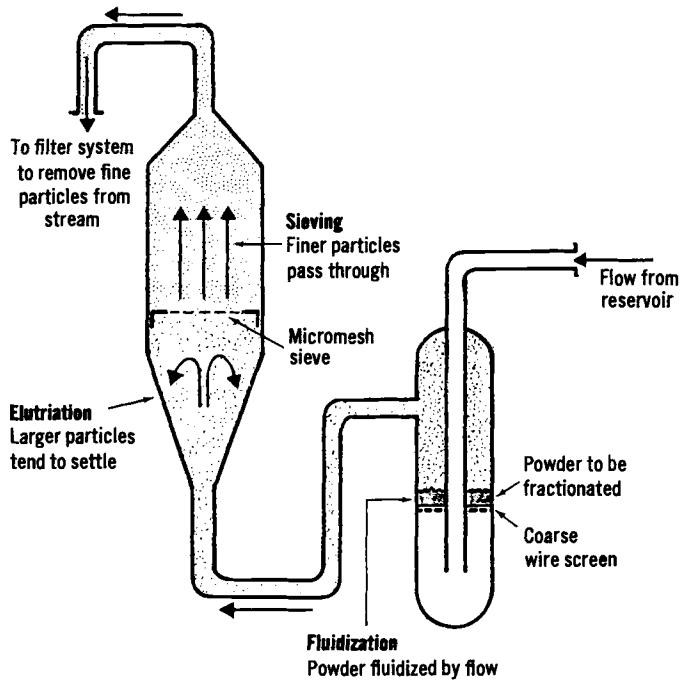


FIG. 10–Felvation. Fractionating powders into different sizes by a combination of fluidization, elutriation, and sieving. (Courtesy of *Chemical and Engineering News*.)

Individual Particle Sensing

In this technology, individual particles are separated from each other by a diluted suspension in either air (by fluidization followed by entrainment in a flowing stream) or a constantly stirred conductive solution. The particles are then forced to pass through the sensing zone. In one air-fluidized instrument, the time of flight between two precisely placed laser light sources and detectors is used to calculate size. In another, the attenuated light as detected by a photodiode is used to calculate a size. In the liquid suspension instrument, a change in the established electrical resistivity through an electrolyte circuit is measured as a particle passes through a small orifice.

Time of Flight from Light Blockage

An instrument based on aerodynamic time-of-flight technology was developed by Dahneke [*31*]. The measurement range is reported to be from 0.2 to 200 μm, with 150 channels per decade and a count rate of up to 100 000 particles per second. Output may be reported in either geometric or aerodynamic diameter. In this instrument, a gas (usually air for pigment particles) is used to break down agglomerate material and entrain them in a controlled flow; a specially designed "pulse-jet dispenser" is used where a controlled flow of air is directed down onto a sample placed into a small cup (Fig. 11). Depending on the nature of the sample, the operator sets the computer values for particle count rate, flow pressure, and pulse pressure. The disperser flow pressure controlling the carrier gas usually remains constant. The disperser

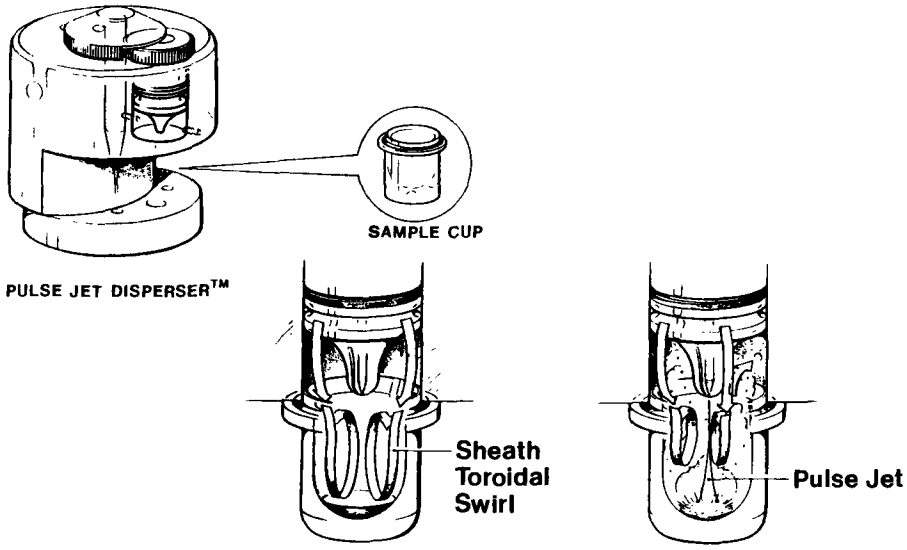


FIG. 11–A diagram of the operation of the dry-powder pulse jet disperser. (Courtesy of Amherst Process Instruments, Inc.)

pulse pressure determines the number of particles fed through the analyzer.

Measurements are made over 2-s intervals to ensure that the minimum count rate is met. Should the count rate fall below the predetermined count rate, the pressure is increased. Should the count rate exceed the maximum allowed, the pressure is dropped by a factor of 2, thus maintaining the number of counts between the allowed maximum and minimum.

The particles are deaggregated to primary size and fed into the injection tube of the sonic nozzle suspended as single particles in the air stream moving at about 6 L per minute. There is no operator involvement during the 1 to 5-min determination. Two laser beams set at a discrete distance apart and directed onto two photomultipliers make up the "sensing zone" (Fig. 12). As the particle passes through the set of laser beams, light that is attenuated and scattered is monitored by the detectors. Signal analysis using cross-correlation techniques give the particle's time-of-flight (TOF) with a resolution of 25 ns. The technique is reported to be able to discriminate between particles with only a 10% size difference. Attachments to the instrument also allow the investigation of sprayed aerosol droplets as well.

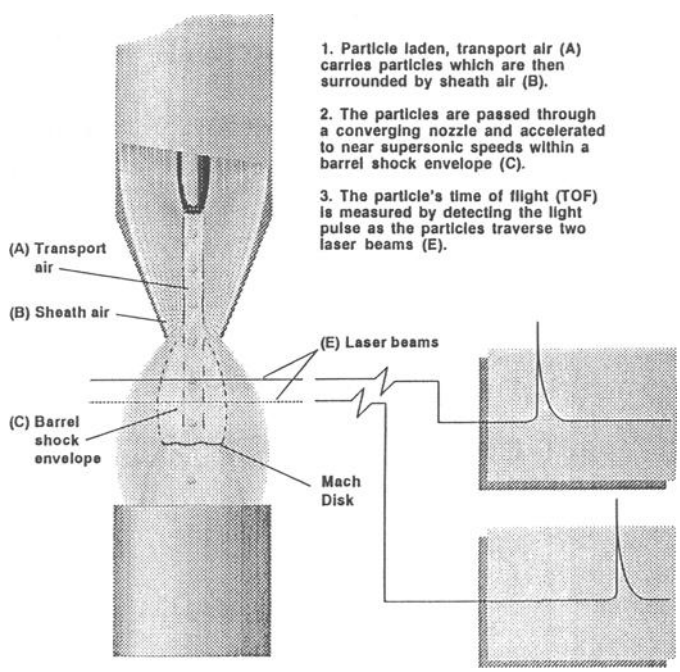


FIG. 12–Schematic of the aerosol beam generator and detection mechanism. (Courtesy of Amherst Process Instruments, Inc.)

Electrical Resistance

According to the Coulter principle [*32-34*], when a particle suspended in an electrically conductive liquid enters a constricted path between electrodes, it changes the pathway electrical resistance between the electrodes. This change produces a fluctuation in the applied voltage that, under proper conditions, is inversely proportional to the volume of the particle. When the dispersion is made to pass through a hole small enough to pass the particles one by one, the resultant series of voltage fluctuations may be electronically amplified, scaled, and counted.

A functional diagram is shown in Fig. 13. The beaker and tube contain the suspension. When the stopcock is opened, a controlled vacuum starts flow of the suspension from the beaker into the tube and also unbalances the mercury in the manometer. The stopcock is then closed, and the mercury siphon continues the flow of the suspension. Electrical contacts in the manometer start and stop the counting of the particles. The volume of the manometer tube between the contacts determines the volume of the specimen. This ranges from 0.02 to 5 mL. A fresh volume is drawn for each count. A typical count requires from 3 to 30 s, depending on the size of the hole and the volume between the contacts in the manometer. The Coulter counter was found to be useful by Princen et al. [*35*] for particle-size determination of emulsified oil systems.

COULTER PRINCIPLE

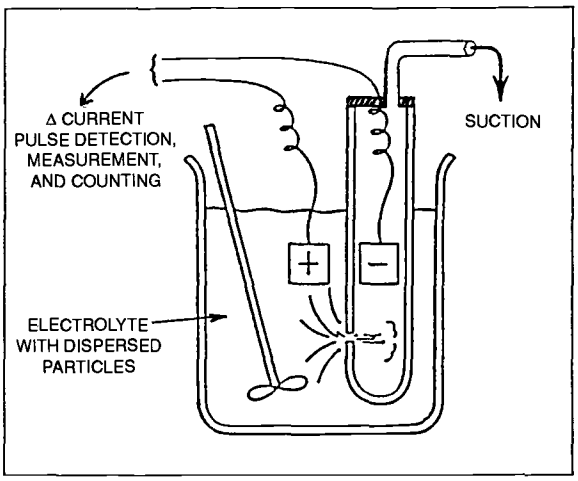


FIG. 13–The Coulter principle: A fluctuation in current flow occurs when a particle paretically blocks the small opening between the electrodes. The size of the particle is related to the amount of change in current flow.

The principle utilized to determine individual particle size is the electrical resistance of the particle as it is forced to pass through a small hole in a glass envelope through which an electrical potential exists.

Particle Size by Sieving

Sieving appears to be a simple means for separating pigments into fractions according to size. A significant addition to the physical laws governing the process has been made by Whitby [*36*], who investigated variables such as size distribution, mesh size, sieve loading, sieve motion, sieve material, and relative humidity. A comprehensive manual on sieving methods has been published by ASTM [*37*] and the W. S. Tyler Company [*38*].

For routine testing, sieves conforming to ASTM Specification for Wire-Cloth Sieves for Testing Purposes (E-11) are useful. These sieves are made of woven wire cloth, supported in frames of up to 12 in. (30 cm) in diameter. A skirt protrudes slightly below the sieve, allowing it to nest into the frame of the next size sieve. The openings in successive sieves progress from a base of 1.00 mm in the ratio of the square root of 2 to 1 (i.e., 1.414:1). When selecting a range of sieves from the series, it is recommended that each sieve, each alternate sieve, or each fourth sieve be taken. In this way, the basic ratio between successive sieves remains constant.

The U.S. Series of sieves is patterned after the Tyler Series that was introduced in 1910 [*38*]. In fact, the two are now interchangeable, the only difference between them being the designations of the individual sieves. Those in the U.S. Series are identified preferably by the sizes of the openings in millimeters or micrometers, while an alternate means is by a number approximately equal to the mesh. Tyler sieves are identified by mesh. Equivalent sieves are available in both series. The sieves proposed as standard by the International Standards Organization (ISO) correspond to many of the sieves in the U.S. Series. Especially useful for sizes under 100 μm is a sieve made by a photoengraving and electroplating process [*39*]. Such sieves are intended to serve mainly as primary reference standards [see ASTM Specification for Precision Electroformed Sieves (Square-Opening Series) (E-161)].

Hand Sieving

If the sieves are used singly, the following directions that appear in several ASTM test methods, among them D 546, Sieve Analysis of Mineral Filler for Road and Paving Materials, may be used.

> After transferring the specimen to the sieve, "Hold the sieve, with pan and cover attached, in one hand in a slightly inclined position so that the specimen will be well distributed over the sieve, and at the same time gently strike the side about 150 times per minute against the palm of the hand on the upstroke. Turn the sieve every 25 strokes about one sixth of a revolution in the same direction each time. Continue the operation until not more than 0.05 g passes through the sieve in 1 minute of continuous sieving."

Sources of error in hand sieving are operator fatigue and casual attention to directions. While machine sieving eliminates these errors, some specifications still require hand sieving unless it can be shown that machine sieving gives the same results.

Machine Sieving

Machine sieving has the advantages of uniformity of treatment and saving time since the operator is free to perform other tasks while the machine is working. Several types of machines are available. The conventional ones impart an oscillating or rotating motion (or both) to the sieve, with regular tapping. None appear to reproduce the motions of hand sieving.

Ro-Tap Sieve Shaker—This machine [*37*] (Fig. 14) manipulates a series of sieves, graduated with respect to mesh size, so as to permit separation of a specimen into sizes. As the name implies, the sieves are given a special rotary motion accompanied at regular intervals by a tap. The nature of the specimen dictates the size of the sieve openings and the timing cycle. This type of machine is recommended in ASTM Test Method for Particle Size or Screen Analysis at No. 4 Sieve (4.75-mm) and Finer for Metal Bearing Ores and Related Materials (E-276).

Sonic Sifter—In the Allen-Bradley sonic sifter [*40*] (Fig. 15), the sieves are stationary, and agitation is imparted to the particles by an oscillating column of air. Sieve wear and particle attrition are said to be minimal. The sonic sifter consists of a sieving chamber, a diaphragm at the top vibrating at 60 Hz, and a motor with the necessary controls. The amplitude of vibration is adjustable to the nature of the specimen. A determination may require no more than 60-s operation of the machine.

To make an analysis, the sieves, in descending order from top to bottom, are assembled in the holder, and the specimen (not more than 30 g or 10 mL) is transferred to the top sieve. The cone, coupling unit, and the diaphragm are added, and the stack is latched within the chamber. The complete assembly is positioned in the machine, the power level and the time interval are set, and the operation is started. After the sift

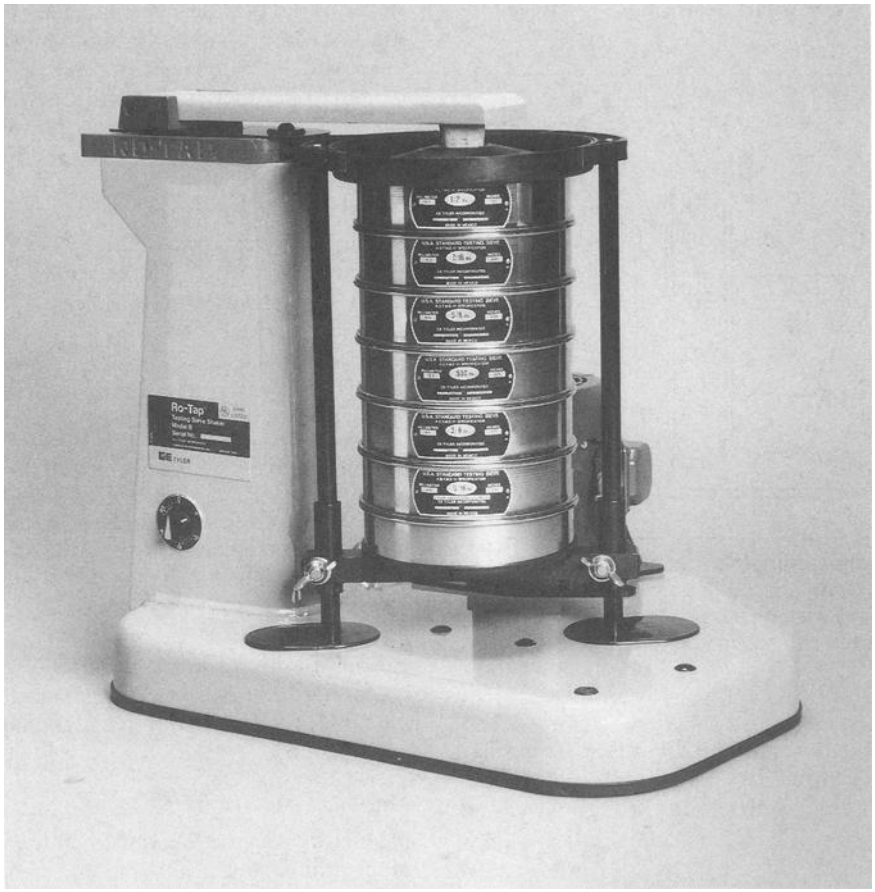


FIG. 14–Ro-tap resting sieve shaker. (Courtesy of W. S. Tyler Co.)

interval, the stack is removed and opened, and the fractions are weighed and computed in the usual manner.

Air-Jet Sieve—A cross section of the air-jet sieve [*41*] is shown in Fig. 16. A specimen is seen being processed through the component parts. The complete operational unit includes a vacuum cleaner. The hose of the vacuum cleaner is fastened to the outlet at the lower left. The specimen is placed on the sieve, and the air, which comes from the rotating split nozzle on its way to the vacuum cleaner, agitates the specimen. The finer particles pass the sieve and are collected in a tared filter bag; the coarse particles are retained on the sieve. Sieves with different meshes are used for additional fractionations, and the procedure is repeated. New tared filter bags are used for each fractionation if retention of the fractions is desired. Air velocity must be regulated, and a manometer is used to indicate the vacuum in the housing.

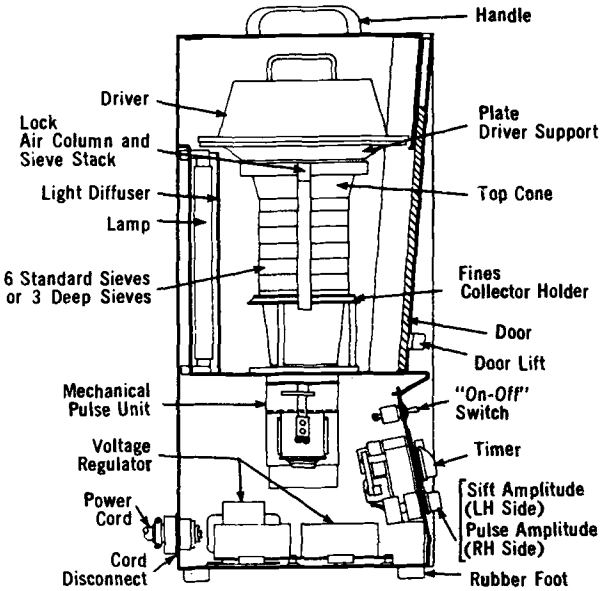
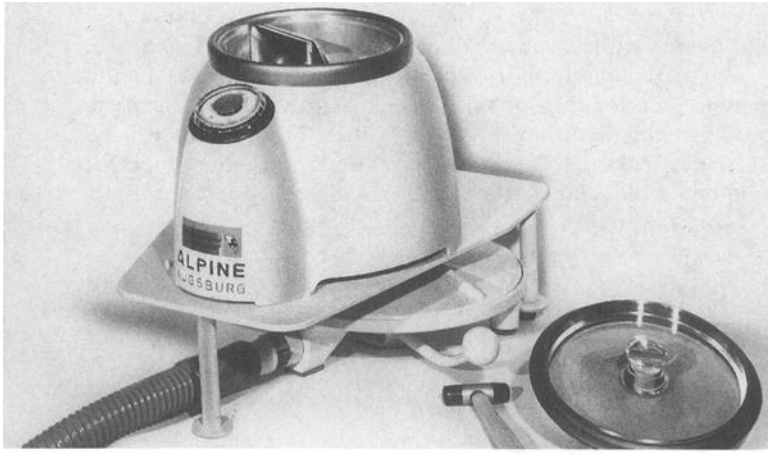


FIG. 15–Diagram of the Allen-Bradley sonic sifter. (Courtesy of Allen-Bradley Co.)

Direct Microscopic Measurement

Microscopes, both optical and electron as well as automated image analyzers, are used to measure particle size directly. Optical techniques suffer somewhat from an inability to focus on the "edge" of a particle at very high magnifications due to a depth of field problem. The lower limit is set by its resolving power and the upper limit by its depth of focus. The microscope is especially useful for measurement of plate-like and needle-shape particles that do not obey Stokes' law, on which the sedimentation methods are based. Disadvantages of the method are that it is slow and laborious. Hence, it is used chiefly for the calibration of the more rapid relative methods. ASTM Practice for Particle-Size Analysis of Particu-



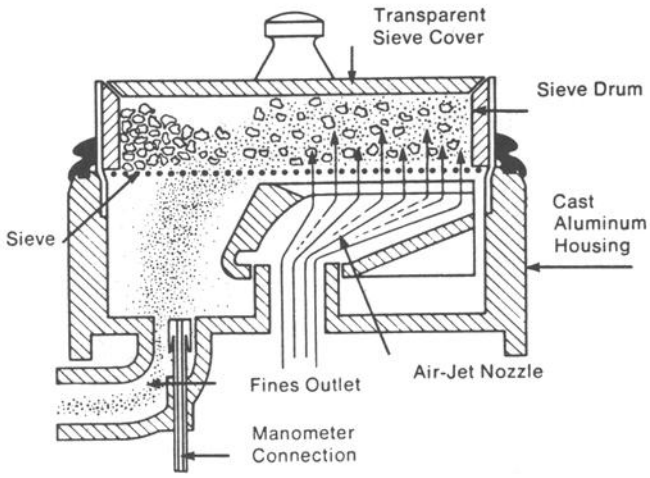


FIG. 16–Alpine air-jet sieve. (Courtesy of Gilson, Inc.)

late Substances in the Range of 0.2 to 75 μm by Optical Microscopy (E 20) and a paper by Loveland [*42*] are good references. Dark field illumination can use the detecting power of the microscope rather than the resolving power for sizes below the resolving power of the optical microscope.

Green [*43*] was the first investigator to systematize the use of the microscope for direct measurement. He dispersed the pigment in a medium on a microscope slide, photographed the dispersion at a known magnification, and projected the image on a screen to increase the magnification for measurement. Dunn [*44*] bypassed the photomicrograph by projecting the image of the particles directly from the slide on the screen.

Ideally, the pigment should be dispersed in the medium in which it is used, but this is rarely done. Green used turpentine, Allen [*45*] recommended a viscous vehicle, and Eide [*46*] used fused resins. Gehman and Morris [*47*] milled the pigment in rubber, dissolved the mix in a solvent, and applied the suspension to the slide.

Microscopes equipped with view-through linear scales, circles or ellipses in graduated sizes, may be used as a direct measurement method [*42*]. The comparison scale may be a micrometer eyepiece, an eyepiece reticle, or a scale engraved on the microscope side.

The use of the electron microscope for particle characterization is now a routine practice. The resolving power is many times that of the light microscope and may be used in scanning as well as transmission mode. With state-of-the-art surface analysis tools such as energy dispersive X-ray (EDX) built into the scanning electron microscope (SEM) equipment, elemental analysis of a single-pigment particle within the coating matrix can be done conveniently while the coating sample is in the instrument.

Array Method Using Optical Microscope

The array method of particle sizing lends itself to systems of monodispersed spheres, as in Fig. 17 (from Duke [*48*]). These are highly uniform with respect to diameter. When placed on a flat plate, the spheres tend to align themselves into hexagonal arrays. These are characterized by straight rows of the particles. Because of this, the rows can be measured, and the diameter of the particles may be derived by dividing by the number in the row.

Transmission Electron Microscopy (TEM)

TEM is useful for the measurement of latex microspheres of 200 nm and larger [*49,50*]. The procedure usually utilizes the magnification factor of the microscope in the size determination from photomicrographs. Because this factor is not always dependable, photographs are sometimes made against a replica diffraction grating of known spacing. Figure 18 shows 100-nm latex microspheres on a 2160-line/mm grating. Sources of error include uncertainty in the accuracy of the line spacing, the roughness of the lines, and the line thickness relative to the size of the particles. Duke [*51*] has used an internal standard of NIST traceable materials, as shown in Fig. 19, and reports accurate sizing to as small as 50 nm.

Particle Size by Sedimentation

The use of the principle that a particle will "fall" through a liquid medium at a rate dependent on its diameter (as well as other variables) is a popular sizing technique. By this

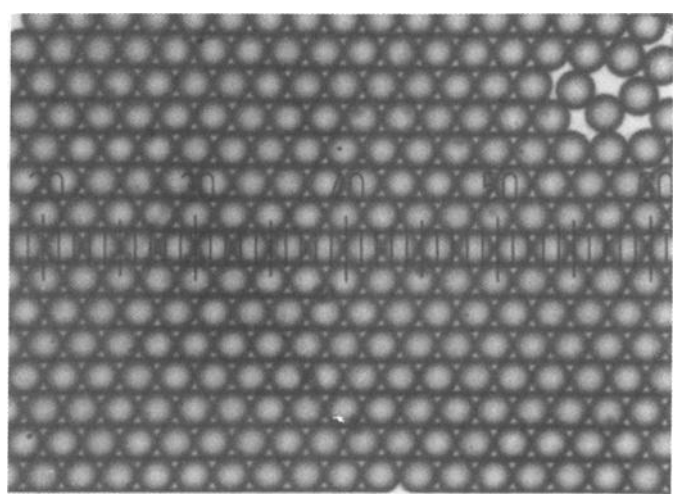


FIG. 17–Microphotograph of 9.87-μm spheres in arrays. (Courtesy of Stan Duke.)

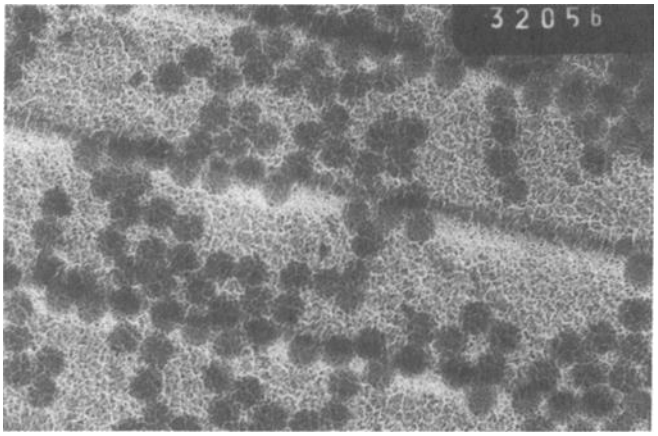


FIG. 18–Microphotograph of 100-nm latex spheres against a 2160-line/mm grating. (Courtesy of Stan Duke.)

method, the pigment particles are dispersed in a liquid and then allowed to settle under the influence of gravity or centrifugal force. The rate of particle movement through the liquid then gives the particle diameter. Among the methods for measuring the rate of particle movement in a fluid are: (1) collecting the particles on a balance pan suspended in the dispersion, (2) analyzing specimens withdrawn with a pipet from different levels, (3) determining density with hydrometers or "divers," and (4) measuring attenuated light transmission through the dispersion. With low-cost computers and extremely stable rotational control provided by advanced electronic feedback circuits, the sedimentation methods using centrifugal acceleration have become popular.

A prerequisite to analysis by the sedimentation process is that the particles must be at their primary size. Vigorous stirring, usually with a dispersant agent or surfactant, both with and without ultrasonics, is often necessary. Agents to prevent flocculation may be required, and adjustments in solution pH may be necessary to stabilize the system. These additives must be evaluated at different levels to determine impact on the derived values.

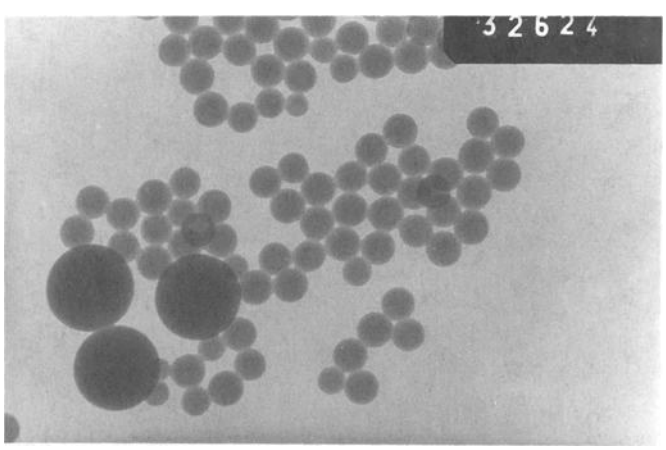


FIG. 19–The use of an internal standard of known size. (Courtesy of Stan Duke.)

Stokes' Law

For essentially spherical particles, one assumes that Stokes' law will be followed when particles are falling in a fluid under some accelerating potential such as gravity or centrifugal force. This assumption requires that the particles will fall freely under laminar flow conditions [*52*]. For a perfect sphere, the diameter can be calculated simply from the Stokes' equation.

$$D = \left[\frac{18\,\mu v}{g(\rho_p - \rho)}\right]^{1/2} \tag{8}$$

where

D = diameter of sphere,
μ = medium viscosity,
v = velocity of fall under influence of gravity,
g = gravitational constant,
ρ_p = sphere density, and
ρ = medium density.

Most often, the particles are not exactly spherical. Because of this, it is difficult to relate a particle's dimensions directly to the observed settling rate. The usual procedure is to use Stokes' equation to determine the values for d from the sedimentation distance and its corresponding time. The value so determined is then the "Stokes' diameter" of the particle. The definition then becomes "the diameter of a sphere that has the same density and free falling velocity (in a given fluid) as the particle being investigated (within the range of Stokes' law)."

This practice avoids the problem of variations in free fall velocities caused by shapes which differ from being a sphere. The assumption holds and permits useful comparisons of the size distributions when similar types of materials are evaluated. The size distribution of particles of different shapes may be compared provided that the phenomenon being studied is dependent on its behavior in the fluid.

While the concept of the Stokes' diameter is useful, it is necessary to appreciate its limitations. One should not equate the Stokes' diameter to a sphere of equal volume or other related quantity. Two types of errors may be introduced. In the first case, errors arise when the particle's movements depart from Stokes' law and, in the second case, errors are introduced by the experimental technique itself.

Departure from Stokes' law can occur when flow conditions are not met. Stokes' equation is valid under laminar flow only. Consequently, there is an upper limit to the size of a particle that can be evaluated in a given liquid. Large particles can experience too high a velocity in the liquid and create turbulent flow. Vortexes in the liquid in the vicinity of other particles also introduce errors. Laminar flow is determined by the Reynolds number experienced by the particle/fluid system at the fall rate. The Reynolds number, Re, is defined as

$$Re = \frac{vd\rho}{\eta} \tag{9}$$

where v is the velocity in the fluid, d is the diameter in centimeters, ρ is density of the particle in grams per milliliter, and η is the viscosity in poise. According to B.S. 3406 [*53*], the value of Re cannot exceed 0.2 if the introduced error from Stokes' law deviation is to be less than 5%. This would imply

that the upper limit of particle size would depend on both the viscosity and density of the fluid. For water, this value would place an upper limit of about 60 μm. However, as might be anticipated from the Reynolds equation, this limit may be stretched somewhat when using either more dense or more viscous liquid media than water.

Another problem arises when the concentration of particles is too great. The Stokes' equation assumes single particles having no influence from the wall of the vessel or other particles in close proximity. Wall effects are minimized by employing properly sized vessels. While some investigators have recommended that the volume concentration should be kept less than 0.05%, others recommend concentrations of up to about 0.5 to 1% by volume. Certain investigators feel that this compromise introduces systematic errors and renders the method inappropriate as an absolute measure, although it is suitable as a routine control method. The flocculating nature of the powder in the test fluid will impact the maximum concentration that can be used. B.S. 3406 recommends a concentration of 1% by volume, although it cautions that, under certain circumstances, a small interference may occur. Because of the potential introduction of systematic errors at higher concentrations, efforts to refine the technique so that reduced concentrations are used are underway. Precision with differentials no more than 4% are usually expected.

Another problem that must be addressed is the temperature stability of the liquid. Not only is there a change in the liquid viscosity, but thermally produced convection currents grossly impact the sedimentation process. Because of the difficulty in maintaining thermostatic control over the long periods required for gravitational settling, there is usually a lower particle-size limit of about 2 μm when water is used as the suspending liquid.

Gravity Sedimentation

The analysis of particles by sedimentation is possible because of Stokes' law, which states that the time of fall of a particle through a viscous medium is proportional to the particle's density (the difference between it and the medium) and its diameter. Of course, if the density of the medium were greater than the particle, the particle would float. Another requirement is that all of the particles must have a common density. This rules out mixtures of different minerals and pigments having different densities since they cannot be determined together.

Because of the time required for sedimentation to occur, the simple gravimetric method and the photometric method appear to be limited to pigments of sizes above 0.5 to 1.0 μm. Cadle [*53.1*] and Orr and Dallavalle [*54*] have reviewed the many variations of the method. Gravity settling was first proposed by Oden [*55,56*]. Calbeck and Harner [*57*] were among the first to use the technique for paint pigments; Jacobsen and Sullivan [*58*] brought the method to a higher degree of refinement by using an analytical balance with one of the pans replaced with a cup submerged in the suspension.

Hydrometer Method—The density of a dispersion is proportional to the concentration of the dispersed material, and methods for particle-size analysis based on the use of the hydrometer have been developed. One such method is ASTM Method for Particle-Size Analysis of Soils (D 422). Another, developed in large part by Bauer [*59*], is TAPPI Method T649sm, Determination of Particle Size of Clay. Included in the method is a nomograph by Casagrande [*60*] to aid in the calculations. The same nomograph is found in Test Method for Particle Size Distribution by Hydrometer of the Common White Extender Pigments (D 3360) [*61*].

Radioactivity Method—Connor and Hardwick [*62*] report on this method for determining the height of the sedimentation. The radioactivity is either induced in the specimen or is used as an external probe. The technique avoids disturbing the suspension by periodic sampling and can be used with both gravity and centrifugal sedimentation.

Centrifugal Sedimentation

The centrifuge is used to provide an accelerating force for sedimentation analysis. Configurations exist using rotating disks with "see-through" ports as well as holders of small see-through cells.

Disk Centrifuge—The technique for the disk centrifuge was developed by Atherton et al. [*63*]. The apparatus might be considered to be a direct descendant of the single cell centrifuge of Donoghue [*64*] and the scratch start technique of Marshall [*65*]. The range is from 0.01 to 0.5 μm.

The apparatus consists of a centrifuge unit, a sampling unit, and an electronic control unit [*66*]. The rotor of the centrifuge is a cell (hollow disk) of plastic or glass that rotates on a horizontal axis (Fig. 20). The back wall is attached to the shaft of the rotor. The front wall has a hole in the middle that serves as an access port. The inside diameter of the standard cell is 10 cm, and the width is 1 cm. In operation, the cell takes liquid up to a minimum radius of 2.3 cm. The speed ranges from 500 to 8000 rpm.

The sampling unit (Fig. 21) consists of a probe connected to collection flask and a clock motor. The probe is an L-shape thin-wall steel tube arranged to rotate about the axis of one arm. The other arm terminates in a sharp bevel for scooping up the contents of the cell in a manner analogous to that of an inside cutter in a lathe. The center of rotation of the probe lies below the center of the rotor.

To make a test, an appropriate volume of "spin fluid," typically a 4% sucrose solution, is transferred to the rotating cell. After swirling stops (20 to 30 s), the specimen—usually 0.5 mL of a 0.5% dispersion—is expelled from a syringe against the back wall near the center of rotation. The specimen flows outward over the wall unit it reaches the free surface of the spin fluid, where it forms a band about 1 mm thick. The spin fluid and the dispersion do not mix because of the higher density of the former. Thus, zero time for the measurement is defined rather accurately.

After the desired time, spin fluid is withdrawn from the cell with the probe, which is driven by a clock motor at 1 rpm. With the pickup end of the probe in the 12 o'clock position, the motor is started automatically. All but 5 mL of the spin fluid is removed for measurement of the undersized fraction of the dispersed powder.

The development of detector systems must consider the action on a transmitted light beam. Light-scattering theory dictates that when light of intensity I_0 attempts to pass through a dilute suspension (i.e., no multiple scattering) of particles, it is lost or extinguished to an extent that I_t makes it

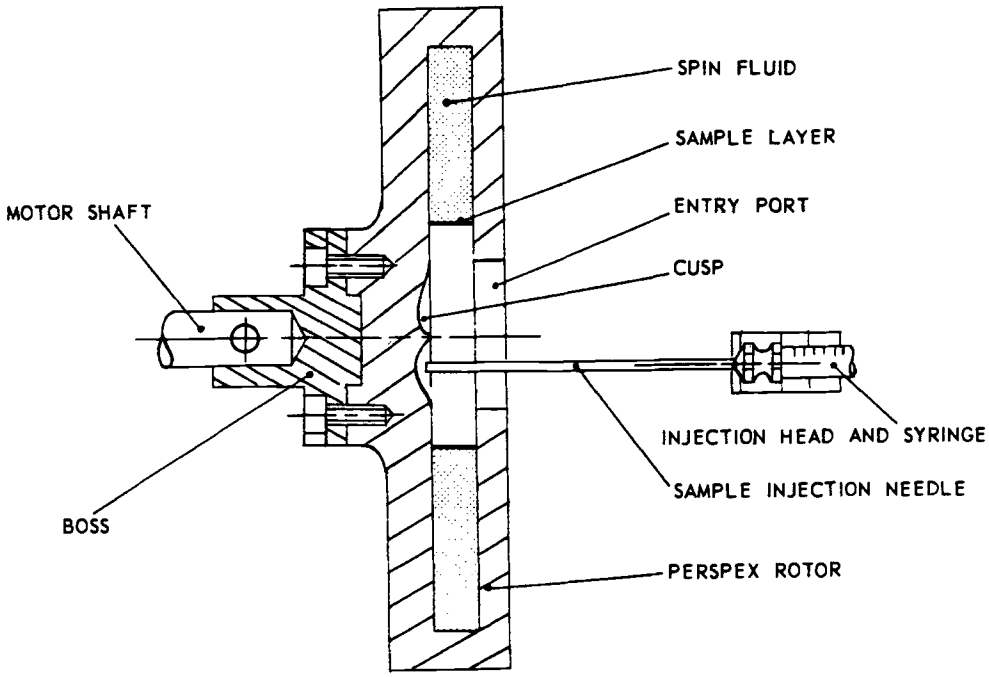


FIG. 20–Diagram illustrating the principle of the disk centrifuge. (Courtesy of Joyce, Loebl & Company, Ltd.)

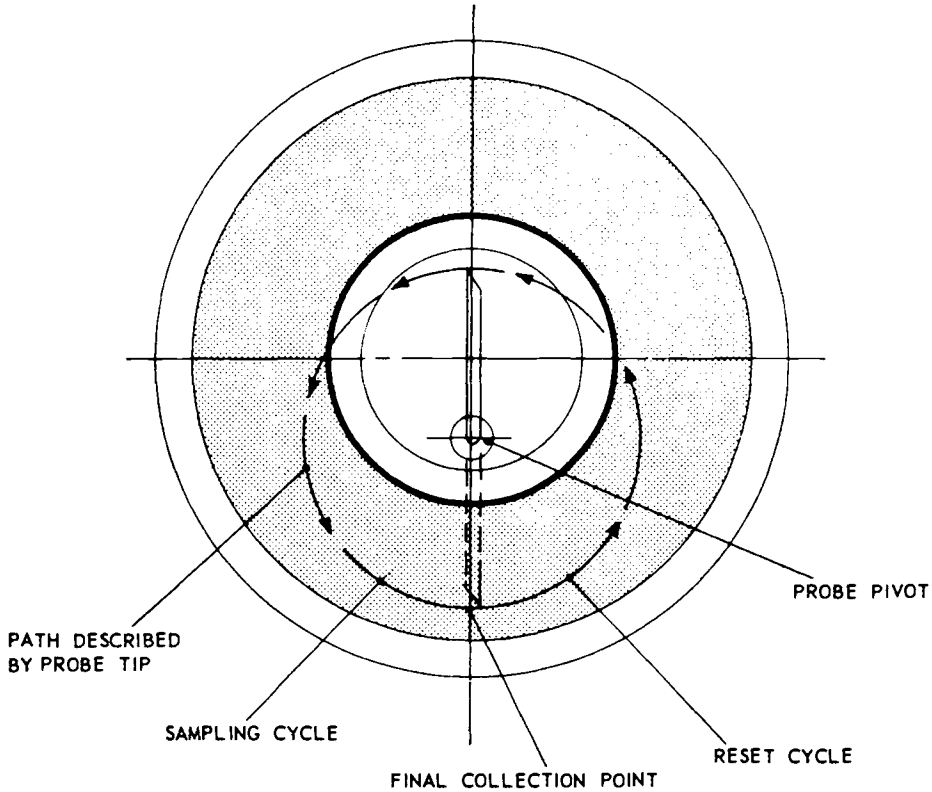


FIG. 21–Relationship of disk and probe of disk centrifuge sampling. (Courtesy of Joyce, Loebl & Company, Ltd.)

through. Mathematically [67,68], the transmitted light is given by

$$I_t = I_0 \exp(-\alpha_{ext} L) \quad (10)$$

where L is the length through the suspension, and α_{ext} is the attenuation coefficient (turbidity). The value of α_{ext} is related to the number concentration of particles, N per unit volume, by

$$\alpha_{ext} = NC_{ext} \quad (11)$$

where C_{ext} is the extinction cross section of the particles. The extinction efficiency of a particle of cross-sectional Area A is conveniently expressed as

$$A = C_{ext}/Q_{ext} \quad (12)$$

This yields the relationship

$$\alpha_{ext} = \frac{N\pi d^2 Q_{ext}}{4} \quad (13)$$

Photo extinction detectors on modern turbidity instruments essentially determine α_{ext}. The internal calculation of Q_{ext} requires knowledge of the particle refractive index, size, shape, orientation, state of polarization, and wavelength of the scattered light as well as the refractive index of the suspending liquid. Using Mie theory [67–69], size may be deduced. Oppenheimer [70] has pointed out that a source of potential error is that the refractive index of the suspending liquid and particles must be known for each wavelength.

Rotating Cell Holder Centrifuge—Real time monitoring is provided on some instruments and is advantageous when irregular measurements force an abort. One such instrument can perform centrifugal as well as gravity analysis using the same on-board computers. With ten different rotor speeds switchable from 300 to 10 000 rpm, an accelerating potential of up to 9000 g is available. Particles as small as 0.01 μm are reported to be measurable.

The instrument uses two small, transparent rectangular cells (Fig. 22) mounted opposite each other on the balanced rotor. While they counterbalance each other, one serves as a reference for the suspension liquid, and the other holds the particle suspension system under analysis. Three photocells in the top monitor three opposite light-emitting diodes (LED) on the back side of the rotor. This allows real-time monitoring of the reference cell, the sample cell, and the rotor speed (Fig. 23). Data are displayed in real time on a built-in CRT as well as printed out on tape after the analysis for a permanent record. Graphs are presented indicating the absorbance versus time, frequency distribution, and cumulative distribution (either percent undersize or percent oversize).

Light Attenuation and Scattering Techniques

Spectrophotometric Techniques

Gamble and Barnett [71] developed a method for measuring particle-size distribution by the scattering of light in the near infrared. The pigment is dispersed in low concentration and placed in a transmission cell for spectrophotometric measurement. From the shape of the spectrophotometric curve, the relative size and size distribution characteristics of an unknown pigment are obtained in terms of calibrated samples (Fig. 24).

Bailey [72] also developed a spectral transmission method using infrared wavelengths from 0.4 to 2 μm. The spectrophotometric curve was related to size by graphic comparison with specimens of known sizes.

Atherton and Peters [73] measured light scattering by polydispersed system of spherical particles. The size distribution curves for the materials compared favorably with direct measurement with the electron microscope.

Leobel [74] used a spectrophotometer to obtain the effect of wavelength on turbidity in the determination of the size of latex particles. The sizes of particles used for calibration were determined from electron micrographs.

Light-Scattering Techniques

When solid particles pass through a light beam, the light will interact with the particles in one or more ways. It can either be reflected, refracted, diffracted, or adsorbed and reradiated. This is shown schematically in Fig. 25. The scattered radiation will present a pattern that is dependent on the shape and size distribution of the particles. By evaluating the scattered radiation detected at different locations relative to the beam direction and in different positions, much can be learned about the scattering media. Figure 26 depicts some of the angular intensities of scattered light produced by particles of various size. With low-cost computers and stable de-

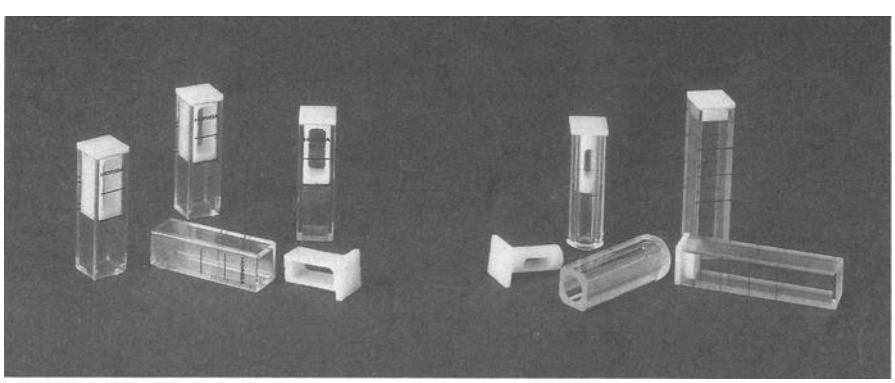
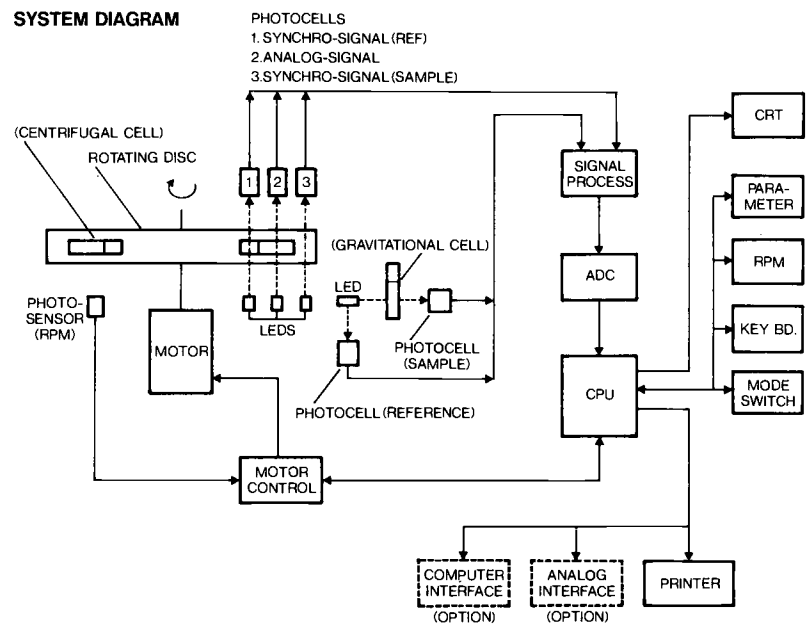


FIG. 22–Reference cells used in a centrifuge. (Courtesy of Horbia Instruments, Inc.)



The CAPA-700 system is comprised of an optical system, a centrifuge, computation circuitry and input/output functions. The rotating disc in the horizontally mounted centrifuge is connected directly to the motor to minimize gravitational effects, and electronic control keeps the rotational speed stable at the set value. The CPU monitors and controls automatic checking for fluctuations in rotational speed, computation formulae and deterioration of the light source and detector, assuring precision data at all times. In the optical system, a reference cell guarantees both optical and mechanical balance for each revolution, which, after CPU processing, gives even higher precision particle size distribution analysis.

FIG. 23–A modern instrument for determining particle size in real time.

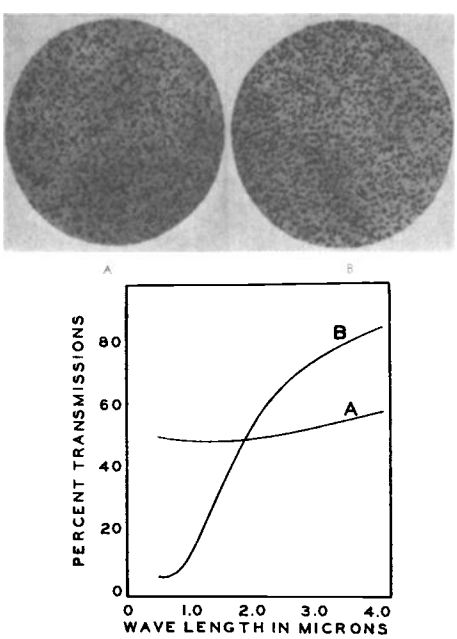


FIG. 24–Particle size may be determined from the scattering of radiation in the near infrared region of the spectrum.

tectors, instruments have been developed that can monitor this scattered radiation, giving fast and reliable data.

Angular dependence techniques, which include detection and manipulation of signals from front (reflection) as well as side and rear (diffraction), have been integrated into a single instrument. Angular-dependence, light-scattering techniques have been widely studied for information concerning the sizes of both pigmentary and nonpigmentary particles. In the latter class, polymeric organic materials from molecular to latex sizes have been included. Debye and Bueche [*75*] described how to characterize the optical inhomogeneities related to size from information concerning the way a system scatters light.

Angular-dependence techniques include the work of Brice et al. [*76*], who designed a photoelectric photometer for measurement of molecular weight by applying the Debye theory.

Aughey and Baum [*77*] note that particles in the size range of large molecules produce variations in the intensity of light scattered at large angles to the illuminating beam. Progressively larger particles produce significant variation in the light scattered at small angles. The light source is a well-defined monochromatic beam. The cell containing the dispersion is stationary, and the photoelectric tube travels around the cell in an arc that covered a useful range from 0.05 to 140°. Scattered light reaches the tube through a small aper-

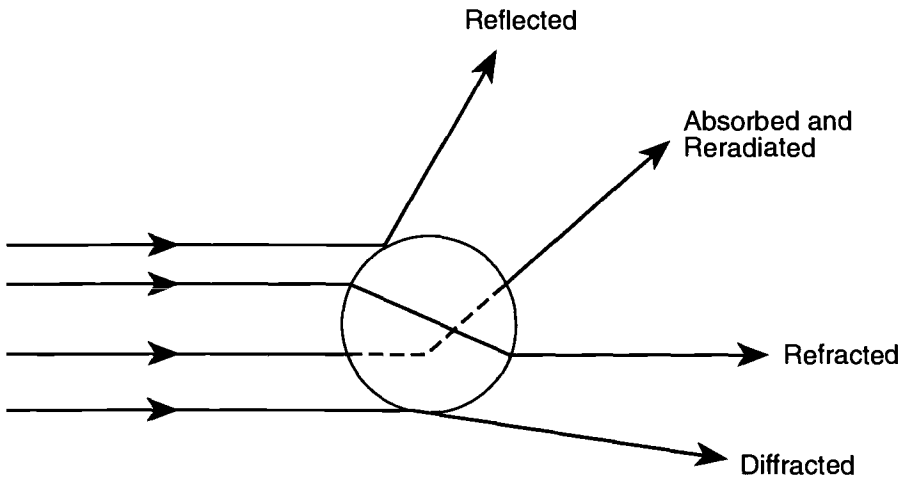


FIG. 25–Possible interactions when light strikes a particle.

ture in the housing for the tube. The radii of the optical inhomogeneities range from 0.1 to 100 μm. Modern diode array detectors are now available to do similar tasks without the movement.

Diffraction of Laser Light—Instruments using diffraction of single-wave-length laser light have been made possible by the development of low-cost, highly stable lasers and diode array detector technology. By fluidizing the particles in a stream of air, they are directed through a cell being illuminated by a laser source. The He-Ne laser, emitting a coherent beam of 632.8-nm wavelength is often used. To increase the cross-sectional area of the beam, expanders are often employed (Fig. 27).

The diffraction pattern that is seen by the detector is a pattern of rings varying in darkness depending on the size distribution of the passing particles. On-board computers use both the Fraunhofer diffraction and Mie scattering theories to calculate the particle-size distribution of the sample. These methods allow the determination of size distribution based on the intensity distribution of the diffracted laser beam. Since the intensity pattern is a function of the actual particle size, mixtures of particles having different densities may be measured together, unlike those relying on Stokes' law. The instrument is reported to address 0.1 to 200-μm particles.

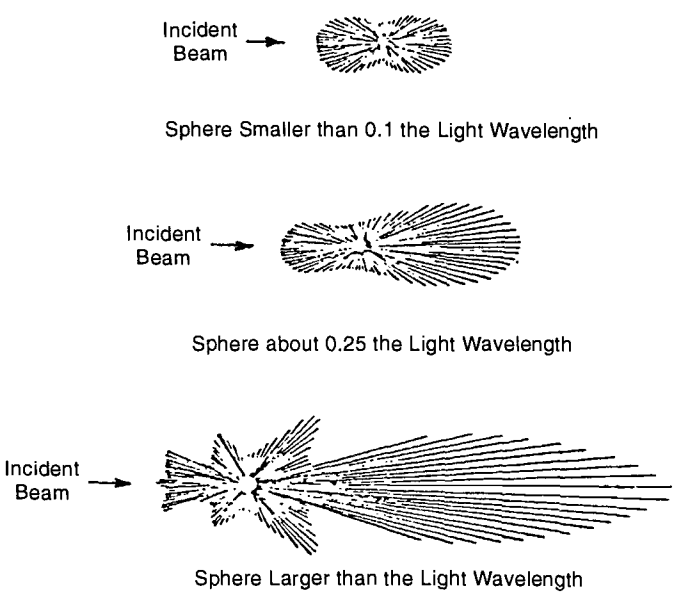


FIG. 26–Angular intensity of scattered light after striking a particle.

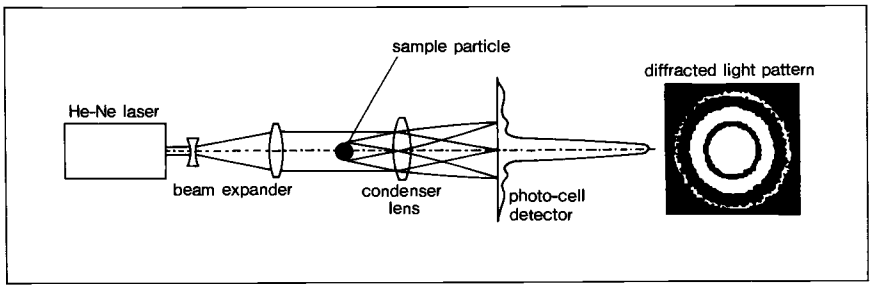
Total Light Scattering—Instruments capable of monitoring light from all sides can effectively measure particles even smaller than the usual limit of 0.1 μm. This limit is imposed because of the physics relating the wavelength of the incident radiation and the interacting particles. By taking advantage of a set of detectors located strategically around the scattering cell, data relating to even very small particles less than 0.1 μm are determined. As the size of the particle decreases, the intensity of the scattered light obscures critical differences in the angular distribution. In practice, this difficulty in treatment of data leads to the so-called laser-diffraction measurement barrier.

Since there is an increase in both the side and rear scattering with very small particles, it is possible to take advantage of the phenomenon. Figure 28 is an instrument diagram with an arrangement of detectors that allow a single instrument to measure a broad range of sizes. Light irradiating the particles is scattered at various angles. For relatively large particles, light is scattered in the forward direction, while, for smaller particles, the light tends to be scattered in all directions. By arranging a lens system and manipulating data from the detectors, the particle-size distribution is calculated from the Mie theory. Since the size of the particles measured is a function of the wavelength of the impinging radiation, the instrument uses a beam of filtered blue light to expand the range.

X-Ray Scattering

The Debye-Scherrer small angle X-ray scattering technique for observing interference effects related to particle size is well known [*78*]. Some generalizations on the use of the technique were addressed by Debye [*79*].

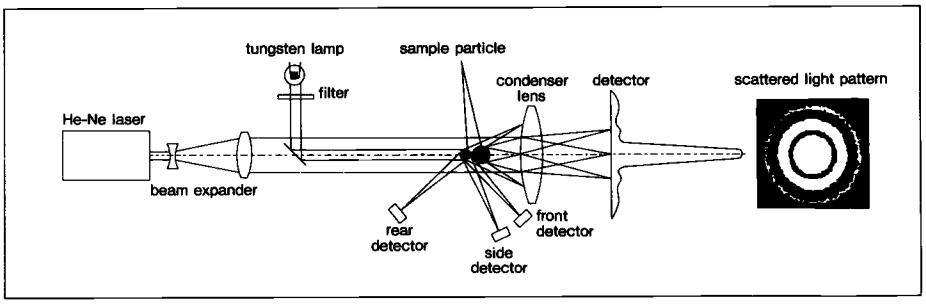
Yudowitch [*80*] and Danielson et al. [*81*] both employed the "diffraction peak" procedure for the determination of latex particle size. For control they used a latex whose size had been determined under the electron microscope.



Principle of Operation

The He-Ne laser emits a beam of 632.8 nm whose flux is enlarged by a beam expander and radiated upon the particles suspended in the liquid. After it has been diffracted and dispersed by the particles, the laser beam passes through the condenser lens and its image is formed at the photo-cell detector located at the focal point of the lens.

The diffraction pattern that appears at the detector is a pattern of light and dark concentric rings that corresponds to the particle size distribution of the sample. Now, using both of the Fraunhofer diffraction and Mie scattering theories, the intensity values are used to calculate the particle size distribution of the sample.



Here is how the LA-900 works.

Light irradiating the particles is scattered at various angles. If the particles are comparatively large, this scattering tends to be concentrated in a forward direction. As the size of the particles decreases, the light is scattered in all directions. Therefore, to measure larger particles, data from a small angle of scatter is required; to measure smaller particles, a larger angle of scatter is required.

On the LA-900, to measure the distribution of low angle scattered light, a condenser lens is used with an array detector at the focal point of the lens. To measure large angle scattered light, detectors are used at the front and rear of the sample chamber. From angular measurement of the scattered light by all of these detectors, the particle distribution is calculated from Mie theory.

It is also true that as the wavelength of the light becomes shorter, so does the measurement size of the particles. Therefore the LA-900 uses a He-Ne laser beam and a red light beam and a blue light beam obtained by filtering a tungsten lamp to expand the measurable range.

FIG. 27–Schematic layout for the large-particle system. (Courtesy of Horbia Instruments, Inc.)

Drawdown Techniques for Texture and Oversize

During the manufacturing of paints and coatings, there is a need for rapid, "on-the-floor" testing to determine whether a dispersion has reached its maximum grind. The "grind" gages were developed to provide quick, on-the-spot answers. Some of the tests could be done in the factory at the disperser during the grinding stage of production. Actually, during the production of paints and pigmented coatings, the pigments are not ground but are only wet out and dispersed to their "primary" size. This primary size is the smallest possible size supplied from the producer.

Thin-Film Drawdown for Oversize Particles

This test [*82*] is suited particularly for detecting oversize particles that adversely affect the gloss of high-gloss industrial enamels. A 2-mL wet film of the enamel is spread on a

Flow Schematics

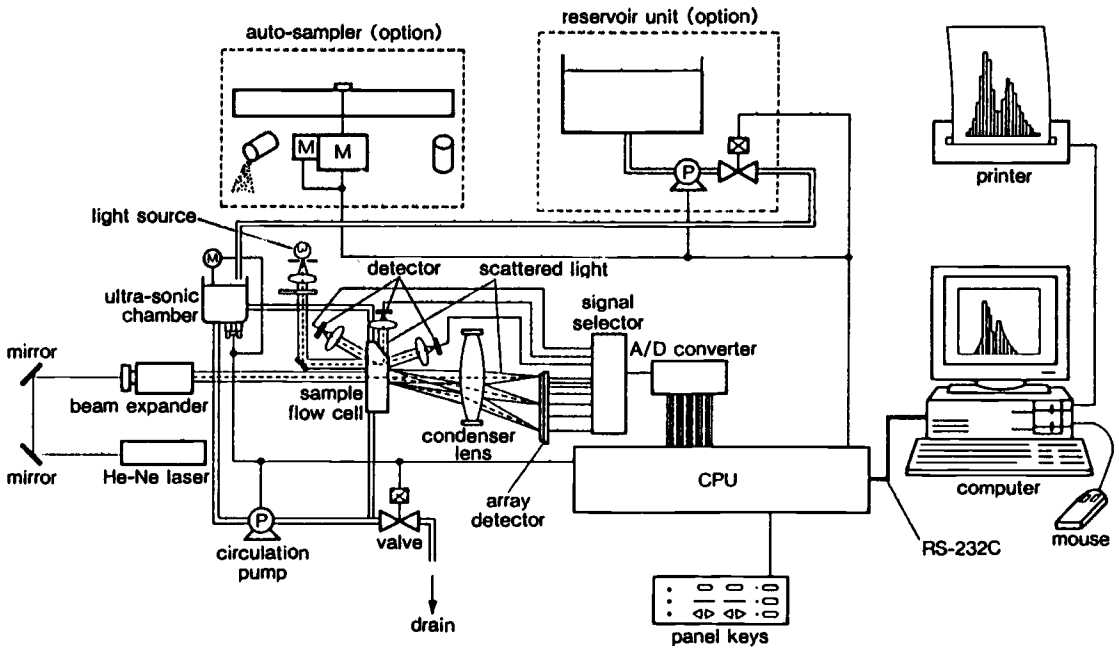


FIG. 28–Schematic layout for a system measuring both large and small particles. (Courtesy of Horbia Instruments, Inc.)

glass plate with a Bird applicator blade. Inspection of the film is best made in a dimly lit room with the operator facing a light source such as a window or under a florescent light with a grid that can be reflected from the wet paint sample. With the eye focused on the silhouetted image of the window sash or the reflected pattern from the light or ceiling, extremely fine particles may be detected and compared with a visual standard. They appear as a roughness to the wet surface.

A variation of this approach is to illuminate the specimen at grazing incidence with a spotlight and view the film through a magnifier parallel to the specimen. Still another version is the use of wedge-shape or step-wise multithickness films.

Fineness-of-Dispersion Gages

Drawdown tests for the detection of oversize particles led to development of fineness-of-dispersion gages, or, as first called, fineness-of-grind gages. The gage is a steel block in which is cut a wedge-shape channel, tapering usually from 4 mils at the deep end to zero at the other end, though other depths and different widths and lengths of the channel are available. Some gages have twin channels. An excess of the sample is placed in the deep end of the channel, and the excess is drawn to the shallow end with a scraper. At some point along the channel, coarse particles or agglomerates become visible. The results are interpreted by reference to standard reference patterns. The addition of slow-evaporating solvents may be required to thin down the system to allow more time for reading the gage without experiencing volume loss by evaporation.

St. Louis Gage—This [*83*], the first of the dispersion gages, was designed to facilitate the use of the North Standards. The channel is 2 in. (51 cm) long and 0.005 in. (0.13 mm) deep at the deep end. The sample and the selected North Standard are placed side by side in the deep end, drawn by a scraper toward the shallow end, and compared.

Hegman Gage—The Hegman gage [*84,85*] (Fig. 29) made the North standards and the St. Louis gage obsolete. It is essentially a St. Louis gage with the addition of a scale to show the depth of the channel or the distance from the deep end. Instead of evaluating the dispersion in terms of the North standards, the distance from the deep end is reported. The finer the dispersion, the greater the distance. This is the reverse of the North standards, where the finer the dispersion, the lower is the number of the standard.

ASTM Gage—The gage specified in ASTM Test Method for Fineness of Dispersion of Pigment-Vehicle Systems (D 1210) is almost identical to the Hegman. The steel block (Fig. 30) is about 180 mm long, 63.35 mm wide, and 12.7 mm thick. The channel is 100 μm deep at the heel. The gage is calibrated according to depth in steps of 10 μm along one edge and to the corresponding nearest 0.1 mil along the other. The dimensions of the scraper are shown in the diagram.

Experience has shown that the speed of drawdowns and the angle at which the scraper is held have no important effect on the results. However, the time lapse between the drawdown and reading, as well as operator technique, are important [*86*]. Readings should be made within 10 s after completion of the drawdown, especially for dispersions with a rating of seven or better due to the volume loss from solvent evaporation. Good practice suggests three drawdowns using

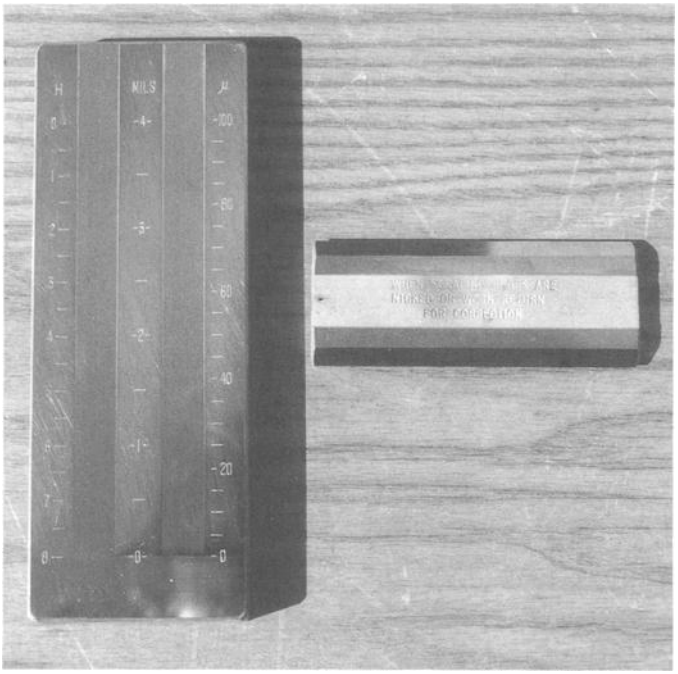


FIG. 29–Hegman fineness-of-dispersion gage. (Compliments of Lynn Shirey.)

fresh material each time. The first drawdown allows accommodation to the light source and a rough estimate of the dispersion pattern and the end point. Subsequent readings may then be made within 3 or 4 s. ASTM directs viewing the drawdown with the line of vision at a right angle to the long dimension of the channel and at an angle between 20 and 30° with the face of the gage in a light that renders the pattern readily visible. Diffuse subdued light is preferred.

Elimination of operator variance is aided by the use of six standard patterns. Figure 31 illustrates reading of the end points, and the scales show the depth of the channel. This scale appears to have some advantage over both the North and the Hegman scales as it is related directly to the dimensions of the oversize particles. Other scales in use include the FSCT (Federation of Societies for Coatings Technology) scale, which divides the distance into ten parts.

Constant Depth Gage—The channels in this gage are of constant depth rather than tapered as in the gages previously described. The gage most often used has four channels, 1/2 in. (1.3 cm) wide and 6 in. (15 cm) long, having depths of 0.002 (0.005 cm), 0.0015 (0.0038 cm), 0.0010 (0.0025 cm), and 0.0005 in. (0.004 cm) equivalent to Hegman values of 4, 5, 6, and 7, respectively. Other depths can be supplied. The advantage of this type of gage is the long path available for inspection, a condition that should minimize the influence of bubbles and foreign matter on the ratings.

NPIRI Grindometer—Printing ink films are much thinner than those of paints or coatings. Relatively fine particles in the latter would be considered relatively coarse in the ink. Because of this, the printing ink range is addressed with a gage designed by the National Printing Ink Research Institute (NPIRI) called the Grindometer [*87,88*]. The channel of this gage is only 0.001 in. deep at the deep end, is 1 in. (2.54 cm) wide, and the scale is graduated in steps of 0.0001 in. (0.000 25 cm).

X-Ray Microradiography Technique

This technique detects undispersed clumps of pigment (inorganic types only) in paint. It uses low-energy X-rays [*89*] to resolve oversize material in the range of 1 μM or less, which is below the range detectable with fineness-of-dispersion gages.

A thin film of paint is spread over the surface of photographic-sensitized, fine-grain film. The specimen is exposed

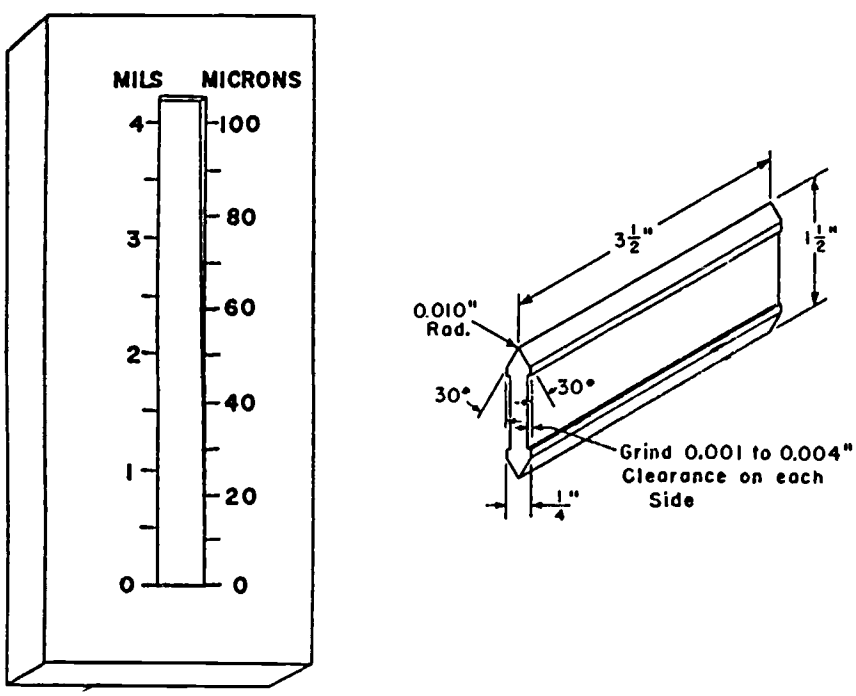


FIG. 30–ASTM dispersion gage and scraper.

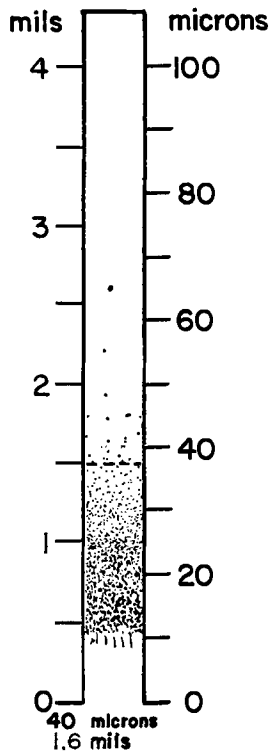


FIG. 31–Typical pattern produced by a dispersion gage.

to X-rays and the film developed after removal of the paint. The film is enlarged optically to reveal silhouettes of the oversize materials on a photographic negative. Determination of size may be made following the methods used for light and electron microscopy.

Hydrodynamic Chromatography: Angstrom Particle Sizing

The separation of angstrom-sized particles may be affected by the use of hydrodynamic chromatography. In this technique, the mixture of very small particles is allowed to transgress a long capillary tube in which the liquid medium is flowing in laminar flow. It is well known that fluids, both gasses and liquids, will experience a pressure drop as a function of distance traveled and of the diameter of the tubing that occurs because the fluid in actual contact with the wall of the tube does not flow and is stationary. For noncompressible fluids, (i.e., liquids), this variation in flow velocity from wall to center of tube may be used to separate particles of differing size.

For laminar flow, the velocity of flow through the cross section of the tube increases from the wall to the center, essentially in concentric "layers" [*90*]. This may be represented by the vectorial diagram in Fig. 32 of the flow velocity profile. The actual velocity of flow of one of the "concentric circular layers" will be a function of its distance from the wall of the tube. The flow velocity gradient is given by

$$V_r = \frac{(P_0 - P_L)R^2}{4\eta L}[1 - (r/R)^2] \qquad (14)$$

where

V_r = liquid velocity at radius, r,
$(P_0 - P_L)$ = pressure drop for the distance, L,
R = inside radius of capillary,
r = effective radius of liquid at V_r,
η = viscosity of fluid in flow, and
L = length of capillary.

Because the larger particles tend to have statistically more volume in the fluid away from the wall, the larger particles are under a greater influence of the faster-moving fluid away from the wall more so than the smaller particles, which can physically fit in the slower-moving layer nearer the wall. Thus, the larger particles advance faster than the smaller ones affecting the separation.

THE ROLE OF PARTICLE-SIZE REFERENCE TEST MATERIAL

Carefully prepared particles of known size and composition have become an important part of testing for emulsions, powders, film, and processes. When properly used, reference particles are an important factor in demonstrating compliance with standards such as ISO-9000, FDA Good Manufacturing Practices and various military specifications [*91*]. In the past two decades, the need for instrument calibration has prompted the establishment of several businesses specializing in the production and supply of reference particles, which are available in assortment of materials of various sizes, densities, and grades.

A brief discussion of some typical applications will illustrate the usefulness of these test reference particles. They are used for instrument calibration, filter checking, flow tracing, and evaluation of processes such as blending, cleaning, and spraying, to name a few.

Instrument calibration and checking covers two broad classes: (1) particle-size analyzers and (2) particle contamination analyzers. Both types of instruments are calibrated or controlled by spherical particle-size standards, primarily polystyrene microspheres, which are normally measured and calibrated by methods traceable to the National Institute of

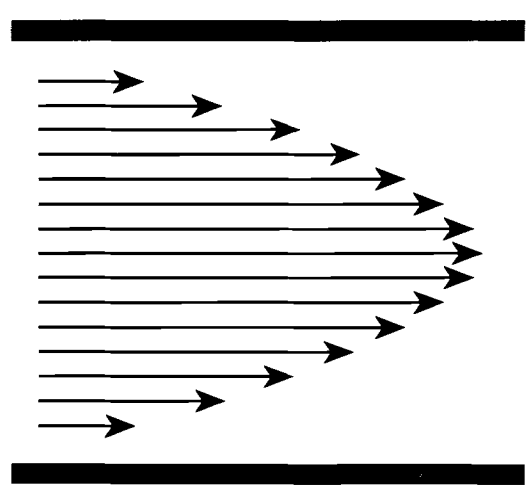


FIG. 32–Vectorial representation of the velocity of a fluid in laminar flow.

Standards and Technology (NIST). The spherical calibration particles have fairly predictable instrument responses and are available as aqueous suspensions of highly uniform particles in discrete sizes (diameters) from 0.02 to 2000 μm. In addition to polystyrene spheres, which may be nonfluorescent or may contain various fluorescent dyes, calibration spheres are composed of silica and glass. Nonspherical materials such as alumina, quartz, and various milled powders are available as experimental materials or controls.

Particle-size spectrometers are used to measure the particle-size distribution of powders, suspensions, emulsions, and aerosols. Other than composition, particle-size distribution is probably the most important variable in product quality and performance. The major class of instruments, particle counters, are used to measure trace amounts of particle contamination in air, water, chemicals, beverages, and medicines. A recent variation of the particle counter can measure particle contamination on flat surfaces, such as silicon wafers, and a variety of optical and electronic parts. All these instruments, as well as optical and electron microscopes, require calibration and reference particles to assure both the quality and traceability of measurements.

In addition to instrument evaluation and calibration, reference particles are used to verify retention ratings and pore-size distribution of air and liquid filter media. Using aerosol particle generators and precision particle counters up and down stream, high-efficiency particulate air (HEPA) filters can be certified for use in ultraclean manufacturing operations for rigorous contamination control. Polystyrene spheres with approximately a 0.25-μm diameter are frequently used for this purpose.

Another broad class of reference particle application is for validating processes, such as for cleaning, blending, dispersing, separation, and spraying. Fluorescent particles, which have bright and distinctive colors that can be contrasted with other background materials, are frequently used to follow the flow or direction of a process. Other materials such as pollens, ground walnut shells, refractory powders, or other materials of the desired particle size and specific gravity are available as model systems for evaluating processes.

In conclusion, reference particles are a key ingredient of modern testing methods, and their use should be considered at an early stage in any QA/QC program as quality management programs require the regular and timely evaluation and standardization of particle-sizing equipment.

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33

Rheology and Viscometry

by Richard R. Eley[1]

Nomenclature

Φ Fluidity integral, Eq 64
α Rate of decay of roughness amplitude, s^{-1}
β Time constant characteristic of a critical shear rate, s
γ Dimensionless shear strain
$\dot{\gamma}$ Shear strain rate, s^{-1}
$\dot{\gamma}_w$ Wall shear rate in tube flow, s^{-1}
δ Phase shift; thickness of adsorbed polymer layer
ϵ Extensional (Hencky) strain, dimensionless
$\dot{\epsilon}$ Extensional (Hencky) strain rate, s^{-1}
η Coefficient of viscosity
η_0 Zero-shear viscosity
η_∞ High-shear limiting Newtonian viscosity
η_d Dispersion viscosity
η_e Extensional viscosity
η_l Liquid-phase viscosity
η_r Relative viscosity, η_d/η_l
η' Dynamic viscosity
$[\eta]$ Intrinsic viscosity (limiting viscosity number)
θ Angle of inclination with respect to the vertical
λ Wavelength of coating surface striations; elastic stress relaxation time constant
ν Kinematic viscosity
π Ratio of circumference of a circle to its diameter
ρ Density
σ Surface tension; generalized stress
σ_0 Initial imposed stress
σ_e Tensile stress
τ Shear stress; viscosity-kinetic time constant for drying, wicking, or thixotropy
τ_0 Yield stress
τ_s Tangential surface shear stress
τ_w Wall shear stress
ϕ Volume fraction of internal (dispersed) phase of a dispersion
ϕ_e Effective volume fraction for a dispersion
ϕ_m Maximum packing fraction of a dispersion, where $\eta_r \rightarrow \infty$
ω Angular frequency ($= 2\pi f$)(rad/s)
A Area of shear face
De Deborah number (λ/t)
F Force
F_g Force of gravity
G Shear modulus
G_∞ Plateau modulus
G^* Complex shear modulus
G' Storage modulus
G'' Loss modulus
K Consistency in power law model; constant in viscosity-molecular weight equation
L Capillary tube length
M_w Weight-average polymer molecular weight
M_c Critical (entanglement) polymer molecular weight
P Pressure
Q Volumetric flow rate
R Capillary tube radius; particle radius; air bubble radius
T Absolute temperature
T_g Glass transition temperature
a Curvature parameter in Eq 15; amplitude of coating surface striations
a_0 Time-zero amplitude of coating surface striations
e Base of the natural logarithmic scale = 2.718 28
f Frequency, Hertz
g Gravitational acceleration
h Film thickness
k Boltzmann's constant; general rate constant
l Length
m Kinetic energy correction term for capillary tube flow, Eqs 72 and 73
n Power law exponent
t Time
v Velocity
x Coordinate parallel to substrate
y Coordinate normal to substrate

INTRODUCTION

THE VALUE OF RHEOLOGICAL SCIENCE is increasingly being realized in the coatings laboratory. One reason is economic: As much as half the cost of new product development can be consumed in solving rheology-related problems of manufacture or performance. Moreover, the rheology of an established product can go awry due to reformulation or a raw material or process change, and such problems are generally in urgent need of solution. Rheological analysis can be a cost-effective aid to the coatings formulator in understanding and solving product and process difficulties.

Traditionally, measurement of the viscosity or "consistency" of paints and coatings had been based on a number of test methods having certain perceived virtues: They were

[1]The Glidden Company (member ICI Paints), Glidden Research Center, 16651 Sprague Road, Strongsville, OH 44136.

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undemanding in operator skill, required inexpensive equipment, and the result was usually a single number requiring no interpretation. These tests proved useful enough, especially as tools of the experienced formulator or bench chemist. This was partly because, in the times when many industrial coatings were solvent-borne and relatively low in solids, the product rheology was seldom far from Newtonian. In the latter case, any test serves as well as any other. The advent of environmentally compliant technologies, such as waterborne, higher solids, and powder coatings, changed this situation. With the new formulations, non-Newtonian, time-dependent, and viscoelastic behaviors were encountered. Here, the traditional methods were inadequate for the reasons that many of the latter tests yield only a single-point measurement, use arbitrary (rather than absolute) viscosity units, or use a flow field which is "nonviscometric."[2] Any of these shortcomings render a method inappropriate for non-Newtonian materials.

A recurrent failing in product viscosity testing is the employment of methods not relevant to the performance property in question. This deprives the test of any analytical or predictive power relative to paint performance. Thus, for example, a low-shear viscosity measured using a spindle viscometer, paddle viscometer, or orifice cup bears no relation to the performance of a paint during application, generally a high-shear process. Part of the aim, therefore, is the development of tests which are related specifically to the critical processes paints must undergo.

Rheological factors play a key role in all stages of a coating's lifetime, from manufacture to the final career of a protective, decorative film. The many processes embodied in that history involve broad aspects of the science of rheology. Table 1 lists some coatings processes, each process having associated with it several distinct deformation characteristics. For each deformation type, a specific rheological test is required to measure its effect on the process. Many of these measurement quantities are independent, i.e., they cannot be inferred from another rheological property. Obviously, if one were to measure only steady-shear viscosity, and over a limited range of shear rate at that, the real cause of a performance problem may be missed. Thus, the characterization necessary for complete understanding of rheology-controlled behavior may require the use of more than one instrument and technique. Notwithstanding, many problems can be solved from shear viscosity and viscoelastic data alone provided the experiments performed are well designed and the results properly interpreted.

In order to take full advantage of the capabilities built into the sophisticated rheological instruments now being widely used in the coatings industry, more than a passing knowledge of the subject of rheology is required. This chapter is therefore somewhat tutorial in style, endeavoring to provide the novice an entry point to the discipline. Certain concepts are discussed at some length because of their importance or complexity. One of these is viscoelasticity. It is worth the time because (a) it is established that viscoelasticity exerts control over coating processes when present, and (b) a number of commercial instruments are capable of viscoelastic characterization of materials.

Finally, in the words of Professor Ken Walters, "Rheology is a difficult subject." This is certainly true, combining as it does several disciplines under one banner: mathematics, physics, physical chemistry, colloid and polymer science, continuum mechanics, etc. This is not to mention the special complexities of the experimental methods used. Furthermore, rheology requires mastery of concepts peculiar to the science with which most persons have had limited opportunity to become familiar in the normal course of a technical education. Nevertheless, it is quite possible for the nonspecialist to acquire a useful working knowledge of the principles and practice of rheology and to use this profitably in linking formulation and performance for coatings.

DEFINITIONS OF BASIC TERMS

Rheology

The derivation of the term *rheology* is from the Greek *rhein*, "to flow." The classical definition of the science of rheology is "the study of the deformation and flow of matter." Some have pointed out a redundancy in this definition since flow is a subset of deformation, as we shall see. An operational definition of rheology would be "the study of the response of certain materials to the stresses imposed on them."

In order to quantify the deformation and flow behavior of materials, three basic terms must be defined. The first two of these relate to the measurement of the deformation (strain and strain rate) and the third to the measurement of the force required to deform the material (stress).

Deformation (Strain)

A deformation is a change in shape and/or volume of a material in response to an applied stress. The equivalent engineering term is *strain*. During the lifetime of a coating, the deformation history may be complex (see Table 1), with the most important components being simple shear and extension. For purposes of definition, we will limit our discussion to simple shear. Simple shear deformation is exactly analogous to the spreading of a deck of playing cards, each card representing a thin volume element (or shear plane) displaced relative to its nearest neighbor (Fig. 1). If a force F is applied to the uppermost volume element (thickness dy), the material will deform by the displacement of adjacent volume elements by a distance dx. The total thickness is Δy, and the total displacement is Δx. The shear strain, γ, is the ratio of the net displacement, Δx, to the distance of separation of the confining surfaces, Δy.

$$\gamma = \frac{\Delta x}{\Delta y} \tag{1}$$

Strain Rate

In order to measure the viscosity, or resistance to flow, of a fluid, we must know not only the extent of deformation (strain), but also the rate of deformation (strain rate). The strain rate is the change in strain per unit time, or the time

[2]"Viscometric" shear flow requires that the flow be "everywhere indistinguishable from steady simple shear" [*1*].

TABLE 1—Rheological components of coatings processes.

Process	Deformation Type or Attribute	Rheological Property	Non-Rheological Effects
Roll Coating	Squeezing flow	Biaxial extensional viscosity	Drying
	Stretching flow	Uniaxial extensional viscosity	
	Shearing flow	Shear viscosity	
	High strain rate	High shear viscosity	
	Large accelerations	Elasticity (G')	
	Large decelerations	G' recovery	
	Surface area transients	Dynamic surface tension	
Spray	High shear rate	High shear viscosity	Flash-off
	Large accelerations	Elasticity (G')	
	High-strain-rate extensional flow	Extensional viscosity/elasticity	
	Surface area transients	Dynamic surface tension	
Brushing/rolling	Medium shear rate	Shear viscosity	
	Stretching flow	Extensional viscosity/elasticity	
	Surface area transients	Dynamic surface tension	
Leveling/sagging	Slow shear flow	Low shear stress viscosity	Wicking
	Surface-stress driven	Dynamic surface tension	Drying
	Transient	Structure recovery kinetics	
Curtain coating	Extensional flow	Extensional viscosity/elasticity	
	Surface area transients	Dynamic surface tension	
	Shear (pumping, extrusion)	Shear viscosity	

$$\text{Shear Stress } (\tau) = \frac{F}{A} \qquad \text{Shear Rate } (\dot{\gamma}) = \frac{dv}{dy}$$

$$\text{Shear Strain } (\gamma) = \frac{\Delta x}{\Delta y} \qquad \text{Viscosity } (\eta) = \frac{\tau}{\dot{\gamma}}$$

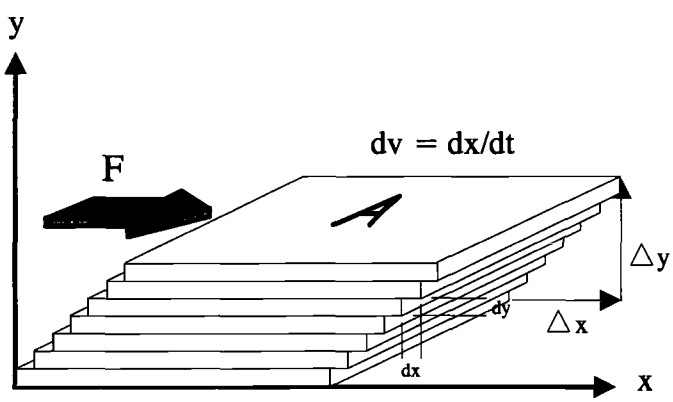

FIG. 1–Basic term definitions for simple shear.

derivative of the strain, symbolized $\dot{\gamma}$, where the "dot" signifies "time derivative of." Therefore, from Fig. 1

$$\dot{\gamma} = \frac{\Delta\gamma}{\Delta t} = \frac{\Delta(\Delta x/\Delta y)}{\Delta t} = \frac{\Delta(\Delta x/\Delta t)}{\Delta y} = \frac{\Delta v}{\Delta y} \tag{2}$$

If the deformation is simple shear, the strain rate is then called the shear rate. The dimensionality of $\dot{\gamma}$ is $LT^{-1}L^{-1}$ (e.g., cm/s per cm). Unit cancellation leaves reciprocal time (s^{-1}) as the unit of shear rate. It is conceptually helpful, however, to remember that, as shown by Eq 2, the shear rate is actually a velocity gradient (change in velocity per unit gap between shearing surfaces, $\Delta v/\Delta y$).

Stress

Force applied to a material creates a state of stress within the material. Stress can be expressed in units of force per unit area (e.g., dyne/cm^2), or, equivalently, energy per unit volume (e.g., erg/cm^3). In terms of Fig. 1, the shear stress, τ, is the force, F, necessary to maintain steady shearing motion against the resistance of the confined fluid divided by the area of the shear face, A.

$$\tau = \frac{F}{A} \tag{3}$$

Viscosity

The viscosity of a fluid characterizes its resistance to flow. The resistance to flow is, in turn, a measure of the friction between the flow units of the fluid (e.g., molecules) or may also be a measure of the attractive forces between the flow units. Thus, a "viscous" fluid (one reluctant to flow) may be so because of high molecular weight (as in motor oil) or be of relatively low molecular weight, but having strong intermolecular interactions (e.g., hydrogen bonds, as between sugar molecules in honey).

The separation of molecules in flow dissipates energy, chiefly as frictional heat. Flow, therefore, is a process which costs energy, of which the viscosity is a measure. For the case of shear deformation, the viscosity, η, is calculated as the ratio of shear stress to shear rate. The viscosity, therefore, is the energy per unit volume dissipated to attain a unit velocity gradient.

$$\eta = \frac{\tau}{\dot{\gamma}} \tag{4}$$

Modulus

Materials comply with an applied stress by deforming, or undergoing strain. For ideal Hookean materials, the strain will be proportional to the applied stress. The modulus is the proportionality constant between the stress and strain. For example

$$G = \frac{\tau}{\gamma} \tag{5}$$

where the shear modulus, G, is equal to the ratio of the shear stress and shear strain. Most polymeric materials and most coatings systems as well are non-Hookean, i.e., the modulus is not a material constant, but will depend on both rate and extent of deformation.

Units

Various systems of units for rheological variables are in use and may be encountered in the literature. Until recently, the most common system of units for rheological terms was the cgs (centimeter-gram-second), or "small metric" system. However, many technical publications and scientific journals now specify that *Systeme Internationale* (SI) units be adhered to. The SI system is based on the "large metric," or MKS (meter-kilogram-second) units, with some additional named units. The units associated with the above variables, according to the various systems, are given in Table 2.

CLASSES OF RHEOLOGICAL BEHAVIOR

Newtonian Fluids

Isaac Newton postulated that the force resisting motion of liquids is proportional to the rate at which one attempts to "separate the parts" of the liquid. In terms of our defined quantities, this would be expressed as

$$\tau \propto \dot{\gamma} \tag{6}$$

or

$$\tau = \eta\dot{\gamma} \tag{7}$$

where η is a constant of proportionality, called the coefficient of viscosity or simply the viscosity.

Equation 7 is the simplest example of a flow model, an expression which allows one to predict the flow properties of a material in response to an applied stress. Fluids which obey Eq 7 over a range of shear rate are said to be Newtonian over that range. The viscosity of Newtonian fluids is a material constant and depends only on the thermodynamic variables of temperature, pressure, and concentration. If the viscosity of such a material is measured at any shear rate or shear stress, the viscosity under all conditions of deformation is known.

Non-Newtonian Fluids

Of materials encountered in the coatings industry, only dilute or low-molecular-weight polymer solutions or stable dispersions of low concentration are likely to be Newtonian. In general, polymer solutions, colloids, dispersions, and suspensions of particulate solids will be non-Newtonian. For non-Newtonian materials, the viscosity is no longer a material constant, but is called a material function—in this case, a "function" of the shear rate (or shear stress). For non-Newtonian fluids, a viscosity measured at a single shear rate is not an adequate representation of the rheology of the system.

CLASSES OF NON-NEWTONIAN BEHAVIOR

In the following sections, the various types of non-Newtonian flow behavior will be outlined. At the same time, several mathematical expressions which can describe non-Newtonian flow will be introduced. Mathematical models are useful for summarizing flow behavior quantitatively. To be sure, materials may be evaluated by qualitative comparison of flow curves (e.g., by visual inspection), but the mathematical analysis of a flow curve has significant value. For one thing, the model constants may have physical significance. For example, some of the models contain a yield stress term (see **Plastic (Yield) Behavior**) as a fitted parameter. The magnitude of this parameter may be coupled to sag or leveling performance [*2*]. A later section of this chapter, **LEVELING,** gives examples of how sagging can be predicted for non-Newtonian fluids using constants from models discussed below. Furthermore, the values of model parameters may be associated with formulation variables, allowing one, in principle, to optimize rheology by adjusting composition in a rational way.

It should be understood that the models about to be discussed are actually idealizations and therefore limited in their ability to represent the behavior of real materials. The models can describe real behavior at least over a limited range of stress or strain rate. Thus, a second use of mathematical models of flow is to make predictions of flow behavior, bearing in mind that it is dangerous to extrapolate the models beyond their range of validity.

As mentioned above, the simplest flow model is the Newtonian expression, which has only one constant, the coeffi-

TABLE 2—Units.

Variable	CGS	MKS	SI
Strain	Dimensionless	...	...
Strain rate	s^{-1}	s^{-1}	s^{-1}
Stress	Dyne/cm^2	N/M^2	Pascal (Pa)(= 1 N/M^2)
Viscosity	Poise (P)(= 1 dyne · s/cm^2) or centipoise (cP) (1 cP = 0.01 P = 1 mPa · s)	...	Pa · s (= 10 P) or millipascal-second (mPa · s)(= 1 cP)
Modulus	dyne/cm^2	N/M^2	Pa

cient of viscosity, η. To describe more complicated behavior, we will have to add additional coefficients and terms, the physical significance of which will be given when possible.

Shear-Dependent Viscosity

Materials in which the viscosity falls with increasing shear rate[3] are designated *shear thinning*. Simple shear thinning behavior without either time dependence (see under **Time-Dependent Fluids**) or a yield stress (see under **Plastic (Yield) Behavior**) is termed *pseudoplastic*, a common type of non-Newtonian behavior in coatings systems. Viscosity rising with increasing rate of shear is called *shear thickening*. The term *dilatancy* (see under **Shear Thickening Fluids**) is often applied to shear thickening behavior, although this refers strictly to shear thickening accompanied by a volume increase, as the term implies. Figure 2 shows curves illustrating viscosity-shear rate relationships for Newtonian and non-Newtonian fluids.

As stated, Newtonian behavior is the simplest of all and is described by Eq 4. The viscosity, η, is a material constant independent of shear rate (Contour *N*, Fig. 2). More complicated viscosity-shear rate behavior requires a more complex expression to model it. The first level of complexity is to add yield behavior (see under **Plastic (Yield) Behavior**) to the Newtonian model, resulting in the Bingham equation [*3*]

$$\tau - \tau_0 = \eta_p \dot{\gamma} \tag{8}$$

Equation 8 says that, above the yield stress (τ_0), the shear stress (minus the yield stress) is directly proportional to shear rate.[4] It is a common misconception that this corresponds to Newtonian behavior above the yield stress. Figure 2, Curve B shows that the Bingham model displays power-law-like behavior, but deviates from the power law (Curve PL) at higher shear rate, approaching the plastic viscosity, η_p, as a limit. Casson [*4*] modified Bingham's equation by taking the square root of all terms

$$\tau^{1/2} - \tau_0^{1/2} = \eta_\infty^{1/2} \dot{\gamma}^{1/2} \tag{9}$$

The Casson model is not empirical, but was theoretically derived specifically for systems whose primary flow units are rigid rods. Casson's equation is reputed to hold for a variety of paint systems, particularly as modified by Asbeck [*5*]

$$\eta^{1/2} - \eta_\infty^{1/2} = \tau_0^{1/2} \dot{\gamma}^{-1/2} \tag{10}$$

which is somewhat surprising since few paints utilize rod-shaped particles as fillers or pigments. In fact, this author's experience is that frequently the Casson model does not represent paint flow as well as certain other models (see below). In Eqs 9 and 10, η_∞, sometimes called the *Casson viscosity*, is not truly an "infinite-shear viscosity," but is a limit that is approached, corresponding to some unknown high shear rate. The value obtained for the Casson viscosity will depend on the maximum experimental shear rate. As with all such models, the user must be aware that the constants resulting

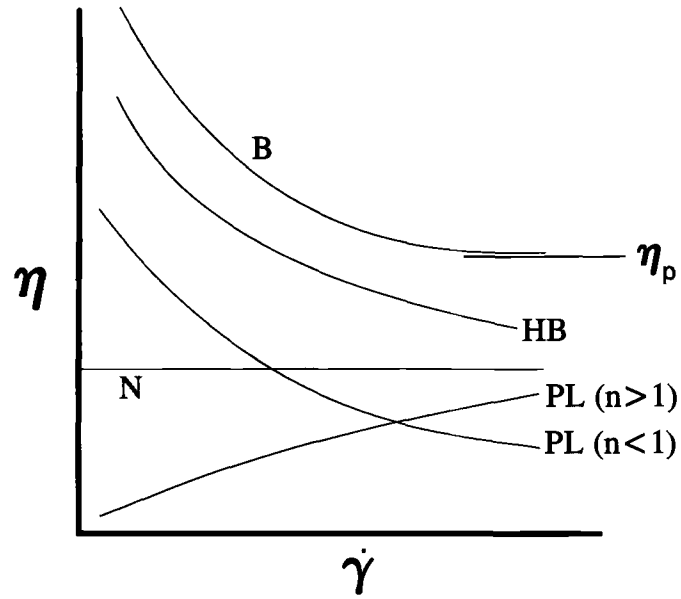

FIG. 2–Viscosity-shear rate curves for simple flow models. Symbols represent the following fluid models: N = Newtonian; B = Bingham (η_p = plastic viscosity); HB = Herschel-Bulkley; PL = power law (*n* = exponent).

from a Casson analysis are not necessarily true material constants. For example, because the analysis of flow data is simply curve-fitting, a finite yield stress will generally be obtained whether or not the material really possesses yield behavior.

The next complication we will introduce is to let the exponent of the shear rate in the Newtonian law be other than unity. In other words, the shear stress now will depend on some power of the shear rate

$$\tau = K\dot{\gamma}^n \tag{11}$$

Equation 11 is known as the power law or Ostwald-deWaele model. Here, K is a constant, sometimes called the "consistency,"[5] which has replaced the coefficient of viscosity, η. This is necessary because the exponent n can be other than unity, in which case K will not have proper viscosity units associated with it. The power law exponent, n, has been termed the "flow index." Its value is characteristic of the dependence of viscosity on shear rate, i.e., whether the viscosity rises or falls with increasing shear. Dividing Eq 11 through by $\dot{\gamma}$ yields a form of the power law which relates the viscosity to the shear rate

$$\eta = K'\dot{\gamma}^{n-1} \tag{12}$$

where $K' = (1/K)^{1/n}$. Obviously, if $n = 1$ in Eqs 11 and 12, the power law reduces to the Newtonian law. A value of $n < 1$ corresponds to shear thinning behavior and $n > 1$ to shear thickening (Fig. 2 curves PL).

The next complication we shall consider is to add a yield stress term to the power law expression

$$\tau - \tau_0 = K\dot{\gamma}^n \tag{13}$$

[3]Any definitions or descriptions of shear rate-dependent behavior may likewise be stated in terms of shear stress dependence.

[4]In the Bingham expression and in other models incorporating a yield stress term, it is important to note that the equations describe flow behavior only when $\tau > \tau_0$. When $\tau \leq \tau_0$, $\dot{\gamma} = 0$ (i.e., $\eta = \infty$), and there is no flow.

[5]Mathematically, K corresponds (in numerical magnitude but not dimensionally) to the viscosity at unit shear rate (1 reciprocal second).

which is known as the Herschel-Bulkley equation. This model describes power law behavior above the yield point (Curve HB, Fig. 2).

Figure 3 shows a generalized equilibrium flow curve [*6,7*]. This figure represents the general features of the shear rate dependence of viscosity for non-Newtonian fluids with any time-dependent or relaxation behavior removed. It consists of a low shear rate Newtonian regime, Region I, an exponential shear thinning regime, Region II, a high-shear Newtonian regime, Region III, and may include a shear-thickening regime, Region IV. The figure is explained in detail (see **Shear-Thinning Fluids**). The chief limitation of the power law models is that they are valid only over a limited range, namely, the linear portion of Region II of Fig. 3. They cannot account for the upper or lower Newtonian regions and, in fact, predict infinite viscosity at zero shear rate and zero viscosity at infinite shear rate, both unrealistic limiting behaviors. Nevertheless, the power law models are found to be quite useful within their limitations, particularly for engineering-type calculations. The Herschel-Bulkley equation has been found to be superior to a number of other models in describing the flow behavior of a wide variety of coatings materials over a useful range of deformation conditions [*8*].

Extending the range of validity beyond Region II in Fig. 3 requires more elaborate models. A simple extension of the power law model is to add an upper Newtonian limiting viscosity, η_∞

$$\eta = \eta_\infty + K'\dot{\gamma}^{n-1} \tag{14}$$

This expression is known as the Sisko model [*9*] and includes Regions II and III of Fig. 3.

Of several proposed models encompassing Regions I, II, and III inclusively, two in particular have perhaps found wider acceptance and utility in the literature. These are the Cross and Carreau models. Hieber et al. [*10*] recently wrote a general form of which the Cross and Carreau models are special cases (here modified to include Region III)

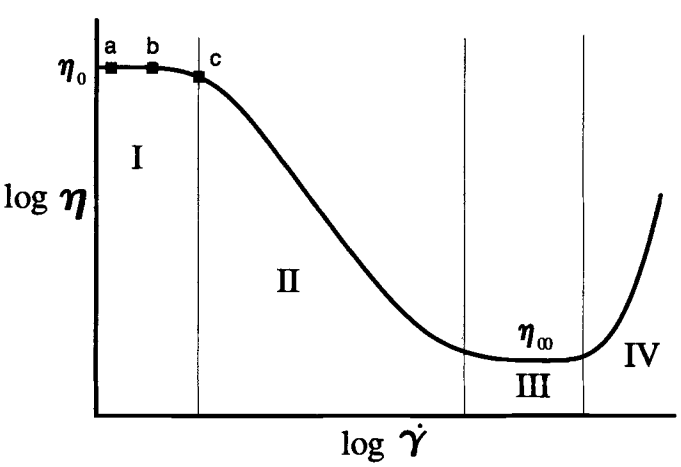

FIG. 3–Generalized equilibrium flow curve: η_0 is the zero-shear viscosity (random structure, maximum disorder); η_∞ is the high-shear limiting viscosity (maximum order). Region I is the first Newtonian plateau; Region II the power law regime; Region III the second Newtonian plateau; Region IV the shear-thickening regime. (Adapted from Ref *6*.)

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{(1 + [\beta\dot{\gamma}]^a)^{(1-n)/a}} \tag{15}$$

Here, η_0 is the first Newtonian plateau viscosity and a is a constant that determines the curvature of the transition region between the lower Newtonian regime and the power law regime. The value of a can be a measure of the breadth of the molecular weight distribution of a polymer [*10*] or perhaps the particle-size distribution of a colloidal dispersion. Setting $a = 1 - n$ in the above expression yields the Cross equation; setting $a = 2$ gives the Carreau-B model. The parameter n has the identical meaning as in the simple power law model (Eqs 11 and 12), i.e., it is the slope of the power law region in a log-log plot of shear stress versus shear rate. The constant β has the dimension of time and is actually a time constant representing a characteristic time of the system. This time constant may be related to, for example, the diffusional or rotational relaxation time of the flow units (be they colloidal particles or polymer chains) or to the time for rupture of particle flocs or aggregates under shear. The location of the transition from the initial Newtonian plateau (Region I) to the shear thinning regime (Region II) in Fig. 3 is governed by the value of β in an inverse sense: increasing β decreases the shear rate of the onset of shear thinning and vice versa. In other words, β defines a characteristic shear rate of transition, $\dot{\gamma}_{tr}$ [*11–13*].

$$\dot{\gamma}_{tr} = \frac{1}{\beta} \tag{16}$$

It is tempting to postulate that β corresponds to the time constant for Brownian diffusion of the primary flow units of a fluid. Stokes-Smoluchowski-Einstein theory gives us the value of β for a particulate dispersion from

$$\beta = \frac{48\pi\eta R^3}{kT} \tag{17}$$

where η is the viscosity of the continuous phase, R is the particle radius, k the Boltzmann constant, and T absolute temperature. For a typical aqueous latex dispersion, $R = 125$ nm, $\eta = 0.05$ P, for which (at 25°C) $\beta = 0.36$ s, corresponding to $\dot{\gamma}_{tr} = 2.8\ s^{-1}$.

When the experimental shear rate equals $1/\beta$, the shear-ordering effect begins to dominate the randomizing effects of Brownian motion, and onset of shear thinning is seen [*14*] (see **Shear-Thinning Fluids**). This event corresponds to Point c in Fig. 3. Equations 16 and 17 show how the transition from Newtonian to shear thinning behavior may be controlled. Any variation which increases the value of β (such as increasing the effective particle size, the continuous-phase viscosity, or lowering the temperature) will move the shear thinning transition to lower shear rates. Decreasing β extends Newtonian behavior to higher shear rates. While Eq 17 is strictly valid only for very dilute dispersions, it still provides qualitative guidelines for manipulating the rheology of dispersions. For concentrated dispersions, η should be taken as the viscosity of the dispersion [*15–17*].

It follows from the above discussion that the broader the size distribution of the flow units, the wider the spectrum of relaxation times and the more gradual the transition from Region I to Region II (corresponding to a smaller value of a).

The shear rate of transition is fixed by β (a *mean* relaxation time), while a represents the *distribution* of relaxation times.

Shear-Thinning Fluids

The term *pseudoplastic* has been applied to fluids which decrease in viscosity with increasing shear rate (or shear stress) and implies shear-thinning behavior without yield stress. However, the term is passing out of use in favor of the more general description *shear thinning*. Particulate dispersions, polymer colloids, and polymer solutions can display this behavior above a certain concentration threshold.

Viscosity is a measure of the dissipation of energy or the "energy cost" to flow. Shear thinning behavior, therefore, implies that an increase of shear rate causes a structural change in the fluid that allows it to flow more efficiently, consequently with less energy loss. The mechanism[6] involves a shear-induced increase in order, or anisotropy, within the system. Thermal (Brownian) motion tends to keep systems disordered (of random order). Shear forces work against this, tending to impose orderliness. If shear rates are low, the randomizing forces win out and the viscosity does not change for small increases of shear rate (Point a to Point b in Fig. 3). Since the structure is no less random anywhere in Region I than at zero shear rate, the viscosity equals η_0, the zero-shear value. As the shear rate approaches a critical magnitude (see **Shear-Dependent Viscosity**), the competition of thermal randomizing and shear ordering starts to favor ordering (Point c in Fig. 3). In the case of polymers in solution, randomly coiled polymer chains tend to stretch in the direction of shear, partially uncoil, and align in more or less parallel fashion depending on the strength of the shear field. The particles of a dispersion tend to line up like "strings of pearls" (Fig. 4) and eventually in ordered planes perpendicular to the shear gradient [*18–20*]. The result is a steadily decreasing viscosity with increasing shear rate as the degree of order increases. Ultimately, if the shear rate is high enough, the maximum amount of shear ordering possible is attained and the viscosity again becomes independent of shear rate (Newtonian).

Figure 3 shows the overall way in which viscosity varies with shear rate for systems such as those described above where Region I is the low-shear Newtonian regime (where Brownian motion controls structure). Region II is the shear-thinning segment of the flow curve (where shear forces control the structure). It is found that the viscosity decreases exponentially with shear rate here; hence, it is often referred to as the "power law" regime. Region III is the high-shear Newtonian regime. Here, the maximum degree of shear ordering has been attained; thus, the viscosity is once again independent of shear rate. The high-shear limiting Newtonian viscosity is usually given the symbol η_∞. Region IV is a shear-thickening region which is occasionally seen, especially with concentrated dispersions. In actuality, shear thickening in dispersions may occur at virtually any magnitude of shear rate depending on dispersion concentration [*21*], so that one or more of the other regimes are obliterated. That is, the equilibrium flow curve may consist of Regions I to IV, I, II, and IV only, I and IV only, or IV only.

Note, once again, that structural order and viscous dissipation are inversely related. An increase in order means decreasing viscosity (Region II), while a decrease in order results in an increase in viscosity (Region IV) [*22*]. It follows that, for Newtonian behavior, no change must occur in structural ordering with shear. If the disperse system is unstable, i.e., tending to flocculate, the dotted curve may be followed (Fig. 5) instead of displaying a low-shear Newtonian regime [*7*]. Some systems may possess an apparent yield stress (see **Plastic (Yield) Behavior**). (See **DISPERSION RHEOLOGY** for additional discussion of particulate system rheology.)

As a general statement, the range of accurate measurement of most laboratory viscometers (for typical coatings fluids) is in the power law region. It may require extraordinary methods or special instrumentation to characterize fluid behavior in Regions I or III.

Shear-Thickening Fluids

We have seen above that shear thinning involves a shear-induced increase in order of a system. This allows the elements of a fluid to move or flow with minimum expenditure of energy. Conversely, shear thickening evidences that shear has caused a decrease in order of a system. The resulting disordered system dissipates more energy during flow and hence is more viscous. An example of this is provided by the catastrophic increase in viscosity observed by Hoffman [*19*], resulting from the "buckling" or "log-jamming" of ordered, layered arrays of particles.

One frequently encountered type of shear thickening behavior is dilatancy. Properly, dilatant behavior is shear thickening accompanied by an increase in volume of the fluid. It is most commonly observed in relatively concentrated disperse systems. In a dilatant system, the disperse phase particles are "wetted" with the minimum amount of liquid continuous phase. Furthermore, at rest, the particles of the disperse phase are in a random close-packed structure for which the interstitial volume is relatively minimal (Fig. 6). If the dispersion moves only slowly, adequate time exists for the meager liquid phase to flow sufficiently to maintain the dispersed phase in a "wetted" state, and the system is able to maintain its close-packed structure. Faster or more forceful motion causes a liquid-starved condition because the interstitial volume increases when the system is deformed or made to flow (Fig. 6). There is no longer enough liquid to lubricate the system. The particles are, therefore, incompletely wetted, and forced flow would ultimately create microscopic voids, leading to fracture of the material. The surface of a dilatant material may appear dry when stressed due to the withdrawal of surface liquid into the increased interstitial volume. This is seen when walking on wet sand on the beach. The resistance to deformation of the material can increase tremendously with increased deformation rate due to these effects.

During the course of a pigment grind operation, a fairly sudden maximum in viscosity is often seen and is an indication that a good grind (i.e., to primary particles) has been achieved. In fact, the surge in viscosity and power draw result

[6]The following discussion applies strictly to "stable" systems, i.e., those in which the net force between flow units is repulsive and therefore which do not flocculate. The shear-thinning mechanism for unstable systems (net interparticle force attractive) is discussed in the subsection entitled *Mechanism of Thixotropy*.

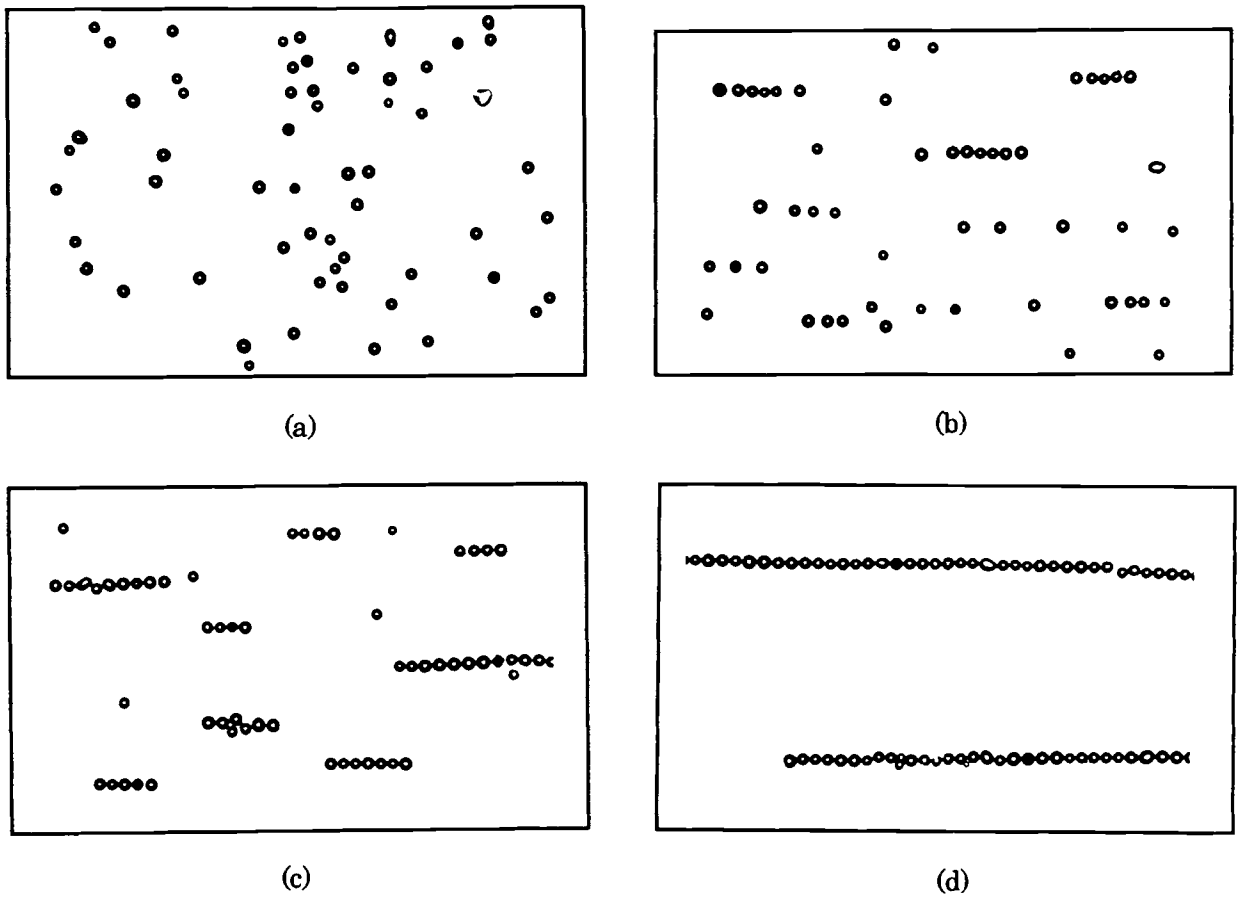

FIG. 4–Dilute suspension of glass spheres in a polymer solution confined between glass plates with small plate separation: (a) just after loading, particles are randomly distributed; (b)-(d) after being sheared in a side-to-side direction at both increasing duration and shear rate. (By permission from J. Michel, R. Pätzold, and R. Donis, *Rheologica Acta,* Vol. 16, 1977, p. 317. Cited in Ref *20.*)

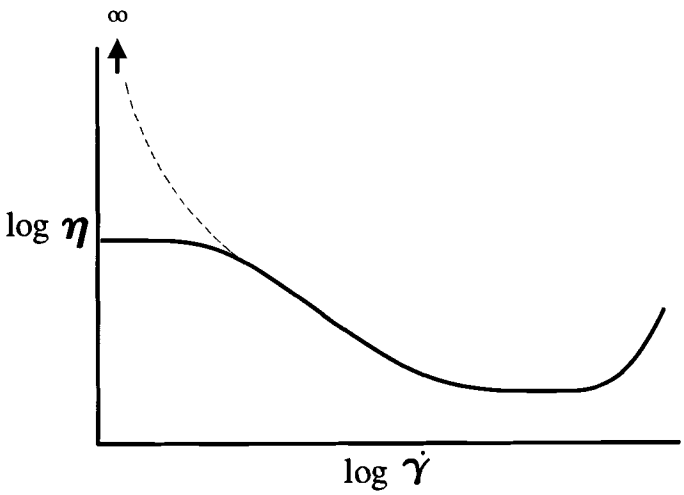

FIG. 5–Flow curve seen for unstable (flocculating) dispersions is indicated by the ascending curve going toward infinite viscosity at low shear rate.

from the grind having become dilatant. The dilatancy is desirable here because it facilitates energy transfer throughout the grind. Thus, dilatancy is frequently an indicator of achievement of a stable dispersion to primary particles. Dilatant systems, in general, are not also thixotropic and therefore permit flow under even very low stresses. For this reason, paints in a dilatant state may suffer from rapid settling and be difficult to redisperse. For most coatings operations, dilatancy is, in fact, undesirable. Pumping of dilatant dispersions may result in high back-pressure in lines, excessive

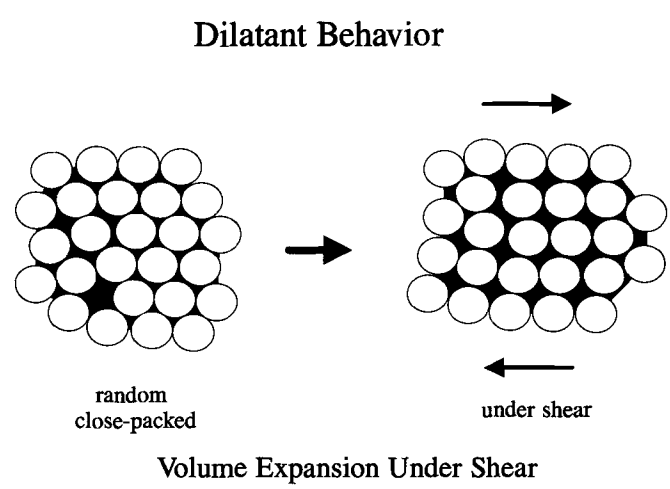

FIG. 6–Dilatant behavior-volume expansion under shear. Random close-packed structure gives way to less-efficient packing with necessary volume dilation.

wear of system components, high power consumption, and loss of metering. In industrial rollcoating, dilatancy shortens coating lifetime on the roll, causing "dry edges" and loss of film thickness control.

Dilatancy is very sensitive to dilution and can be dramatically reduced or eliminated by a small reduction in paint solids. Also, addition of flocculants, electrolyte, a particulate phase of different particle size, or warming can alleviate undesirable dilatancy. Flow curve measurement provides an excellent means of quantifying the degree of reduction of dilatancy achieved by these measures.

Time-Dependent Fluids

Time-dependent fluids are those whose viscosity is a function of both shear rate (or shear stress) and time. The most common such behavior encountered in coatings is time-dependent shear thinning or *thixotropy* [*23*]. At constant shear rate and temperature, the viscosity of thixotropic fluids will fall, eventually reaching a constant value. If the shear rate is changed, the viscosity will approach a new equilibrium value at a characteristic rate. This behavior is illustrated in Fig. 7, showing the way viscosity changes for a time-dependent system when the imposed shear rate (or shear stress) is changed in steps. Initially, the shear rate is zero, and the viscosity is very high or infinite for a thixotropic system. As a shear rate greater than zero is imposed ($\dot{\gamma}_1$), the viscosity drops exponentially, reaching a constant value. Increasing the shear rate to $\dot{\gamma}_2$ decreases the viscosity further to a new equilibrium value. A decrease of the shear rate to $\dot{\gamma}_3$ results in an exponential rise of viscosity to a higher equilibrium value. If, instead of a multiple steady-shear experiment, just described, we were to carry out a shear rate (or shear stress) ramp experiment (Fig. 8*a*), the time dependence would result in a loop (Fig. 8*b*). The explanation of the loop is given below, but has to do with the fact that in a ramp experiment the equilibrium structure is never attained. The circuit in Fig. 8*b* is called a *thixotropic loop*. Roughly bisecting the loop is the equilibrium-structure curve generated from the equilibrium viscosity data of Fig. 7. The analogous time-dependent behavior for

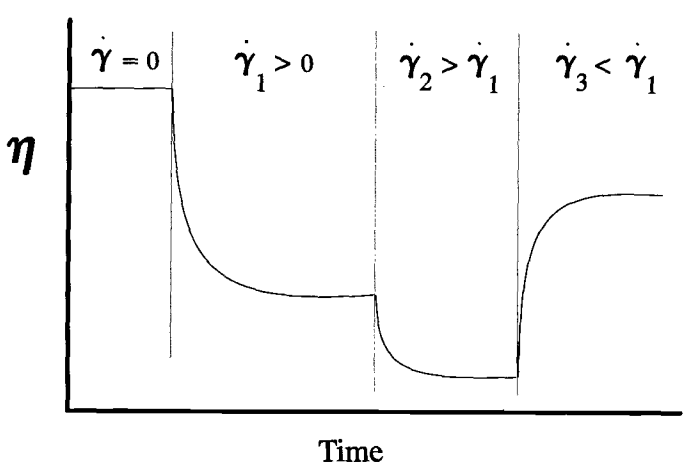

FIG. 7—Time-dependent fluid behavior. At $\dot{\gamma} = 0$, viscosity is high (or infinite). Imposing $\dot{\gamma}_1 > 0$ causes viscosity to fall exponentially, reaching new equilibrium value. Subsequent changes in $\dot{\gamma}$ result in re-equilibration of structure, hence viscosity.

shear thickening materials has been called *rheopexy* (a rather rare phenomenon). The preferred term now for the latter is *antithixotropy*.

"Thixotropic Index" Test

We emphasize that the most important characteristic of thixotropic behavior is not shear thinning alone, but time dependence. The relatively slow change of viscosity provides a means of control of flow behavior and is the reason thixotropy is formulated into coatings. Hence, it is important to correctly characterize the time-dependent aspect of the behavior. For this reason, the so-called "Thixotropic Index" test is of limited benefit for characterization of such systems.

We will digress for a moment to discuss the Thixotropic Index test since it is very widespread in practice. This misnamed test determines the ratio of viscosities measured at arbitrary high- and low-shear conditions. ASTM Test Method D 2196 specifies taking the ratio of viscosities measured on the Brookfield Synchro-Lectric viscometer at two speeds, representing a ten-fold speed ratio. Since only equilibrium viscosities are measured, the test yields no information about time dependence and should be called the "Shear-Thinning Index" instead (it is so termed in ASTM D 2196). Its value, like many quality-control tests, is in its simplicity and "quick-and-easy" character, requiring no interpretation. As long as a given coating formulation changes little, so that the hidden kinetic factor would be expected to change little, the "Thix Index" can reveal when something has gone awry (i.e., can be useful as a gross indicator whether a formulation error has occurred). However, it is always possible that the recovery kinetics of the system have changed, which would go completely unnoticed if the "Thix Index" were the only test used to evaluate the rheology. Below, we will present test methods which can be virtually as simple as the "Thix Index," but which give more useful, relevant, and complete information about thixotropic systems.

Mechanism of Thixotropy

Thixotropy is formally defined as an isothermal, reversible sol-gel (fluid-solid) transformation [*24*]. As stated, it is experienced as a viscosity which is both time- and shear-dependent. Its origin is the breakdown, under shear, of internal fluid structure to smaller flow units or the reassembly of structure from smaller units when shear is relaxed.

The mechanism of shear thinning in thixotropic (time-dependent) systems is different from pseudoplastic (time-independent) systems. In pseudoplastic systems, shear thinning is the consequence of order externally imposed by shear [*14*]. In thixotropic systems, an internally imposed, viscosifying structure exists at rest, and the viscosity falls because of the collapse of that structure under shear. (Flocculated systems possess extra mechanisms of energy dissipation [*25*]; therefore, their viscosity will be higher than that of a deflocculated dispersion of the same composition.) A further important difference between the two is in the amount of time the structure requires to respond to changes in shear rate. In the case of time-independent systems, rapid structural equilibration quickly accommodates to changes in shear rate. The accommodation process essentially is particle diffusion, which is quite rapid for submicron particles (see **Shear-Dependent Viscosity**). The viscosity (a measure of structure)

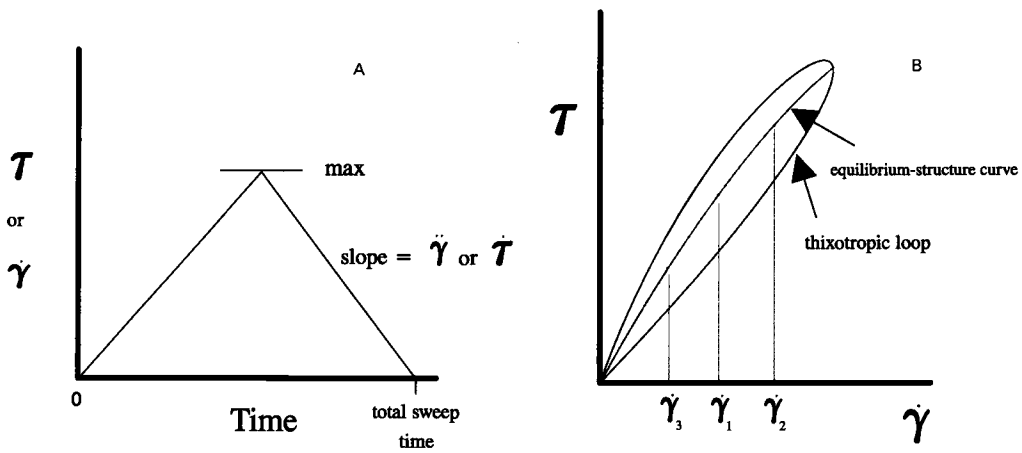

FIG. 8–(A) Shear rate or shear stress ramp experiment. Shear rate or stress increases linearly (sometimes logarithmically, optionally) to preselected maximum over a selected sweep time period, resulting in a given acceleration gradient ($\ddot{\gamma}$) or stress rate ($\dot{\tau}$); (B) Thixotropic loop. Equilibrium structure curve (approximately bisecting loop) corresponds to data from an experiment like that in Fig. 7.

thus always "keeps up" with changes in shear rate for such systems. For thixotropic systems, the rate of structural reorganization is slower than the experimental rate of change of shear rate ($\ddot{\gamma}$) or slow with respect to the time of observation at constant shear rate. In a "shear rate ramp" experiment (see below), the structural breakdown always lags behind the ever-increasing shear rate, so that the viscosity on the "up" ramp will be higher than the equilibrium viscosity at a given shear rate. On the "down" side of the ramp, the rebuilding structure lags behind the rate of reduction of shear rate, so that the measured viscosity is always lower than the equilibrium value. Thus, a "thixotropic loop" is seen, the size of which should be proportional to the structural time constant for a given ramp time. Holding the shear rate constant, as in the description above, allows the structure breakdown process to "catch up." The viscosity then continues to change until an equilibrium between structural breakdown and recovery rates is achieved (see Fig. 7).

Thixotropy Test Methods

Two common test methods for experimental characterization of thixotropy are the "Thixotropy Index" test, and the "Thixotropic Loop" test, described above. In the latter, a programmed increase and decrease of shear rate (or shear stress) is applied to a material (Fig. 8*A*), resulting in the generation of a loop (Fig. 8*B*). The size of the loop can be obtained by numerical integration and is taken as an indicator of the rate of structural breakdown and recovery for a given ramp time (the larger the loop, the slower the breakdown-recovery rates). This method is a difficult one to do correctly, however, and is more complex than first appears. The result (loop size) depends on the shear history of the sample—the time interval since its last shear experience—and the magnitude of the shear undergone. It also depends on the shear rate (or shear stress) maximum in the loop experiment and the ramp rate ($\ddot{\gamma}$ or $\dot{\tau}$).

A better method is one which puts the thixotropic material into a known state, i.e., having had a controlled shear experience, followed by the test. Such a method is the step-shear

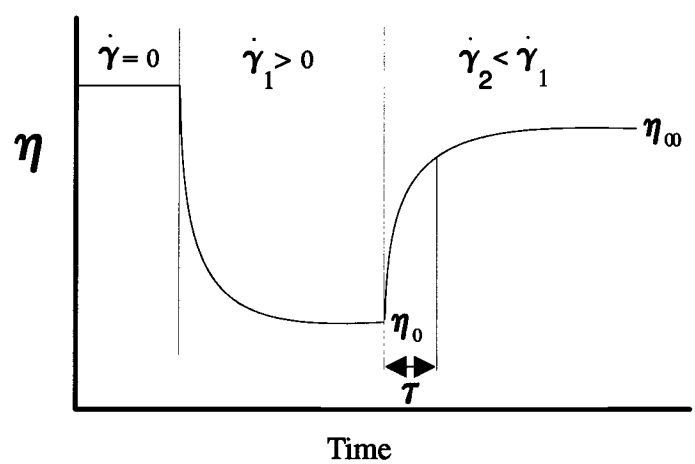

FIG. 9–Step-shear method for thixotropic recovery. High shear rate $\dot{\gamma}_1$ simulates application process, followed by low shear rate $\dot{\gamma}_2$, emulating film after application. Viscosity recovers from zero-time value $\eta_{(0)}$ with a characteristic time constant τ, eventually reaching final level $\eta_{(\infty)}$.

test (Fig. 9). In it, a high shear rate (order of 10^4 s^{-1} desirable) is applied to the material, allowing time for the viscosity (hence, structure) to reach equilibrium; then the shear rate is suddenly reduced to a very low value (order of 1 s^{-1}). The equilibrium amount of structure which can exist at the lower shear rate is greater than at the previous high shear rate, so reassembly of fluid structure occurs, accompanied by an approximately exponential rise of viscosity. Meaningful physical constants can be extracted from the data by fitting the following equation to the recovery curve

$$\eta(t) = \eta(0) + [\eta(\infty) - \eta(0)][1 - e^{-t/\tau}] \qquad (18)$$

where $\eta(t)$ is the viscosity as a function of time, t, $\eta(0)$ the sheared-out viscosity (at time zero), $\eta(\infty)$ the infinite-time recovered viscosity level, and τ the time constant describing the recovery rate. The ratio $\eta(\infty)/\tau$, which we have termed the *Recovery Parameter*, has been found in our laboratories to correlate well to thixotropy-related properties such as sag

TABLE 3—Gel coat thixotropy test data comparison: τ is the recovery time constant and $\eta(\infty)$ the recovered viscosity level from a step-shear experiment; $\eta(\infty)/\tau$ is the recovery parameter.

Composition	τ, s	$\eta(\infty)$, P	$\eta(\infty)/\tau$, P/s	Thix Index	Sag?
With additive	8.9	116	13	4.04	No
Without additive	18.2	97.3	5.4	4.24	Yes

resistance and air entrainment [*26*]. Table 3 shows data for two gel coat formulas, one sagging and one nonsagging. The conventional "Thix Index" results do not predict the sag behavior and, in fact, are opposite what would be expected from the observed behavior. The step-shear experimental parameters τ and $\eta(\infty)$ are given, along with their ratio. The nonsagging formula ("with additive") has both a shorter recovery time and a higher final recovered viscosity, and the recovery parameter takes both of these into account to predict significantly better sag resistance than for the "without additive" material.

The step-shear test puts useful thixotropy characterization within reach of any development lab, for it can be performed on an inexpensive viscometer (such as the Brookfield Synchro-Lectric or Wells-Brookfield Cone/Plate Viscometer) as well as on more sophisticated instrumentation. The latter offer advantages, of course, particularly if possessing viscoelastic characterization capability. The ideal way to characterize thixotropic recovery is to break down the structure under high, steady shear (as in the step-shear method), then step down to a small-amplitude (small strain) oscillatory-shear test, as described by Dodge [*27*] (Fig. 10*a*). The rebuilding of structure can then be followed by means of the viscoelastic parameters, which are sensitive probes of the fluid structure responsible for thixotropy. This method more faithfully mimics processes occurring in the relatively quiescent film after application. Figure 10*b* shows the recovery curves of the viscoelastic moduli G' and G'' (see *The Viscoelastic Parameters and Their Measurement*) from such a step-shear experiment.

Plastic (Yield) Behavior

An ideal plastic material behaves as an elastic solid until a critical stress is applied, whereupon it will "yield" and become fluid. This critical stress is the yield stress, the minimum stress necessary to initiate flow. Ideally, the properties of a material exhibiting yield behavior would be those of an elastic, or "Hookean," solid, below the yield stress. For such materials, the steady-shear viscosity would be infinite (or undefined), the deformation linear with stress, and the yield value a material constant. For most real materials, however, deformation below the yield point is a combination of elastic strain and viscous flow. This is because interparticle forces ("secondary bonds") are of a range of types with a corresponding range of relaxation times [*28*]. As a consequence, the measured yield value will depend on the rate at which the stress is increased up to the point where flow occurs (the faster the rate of stress increase, the higher the measured yield value).[7]

[7]For this reason, yield stress values cited in the literature are meaningless unless the exact experimental methodology is provided.

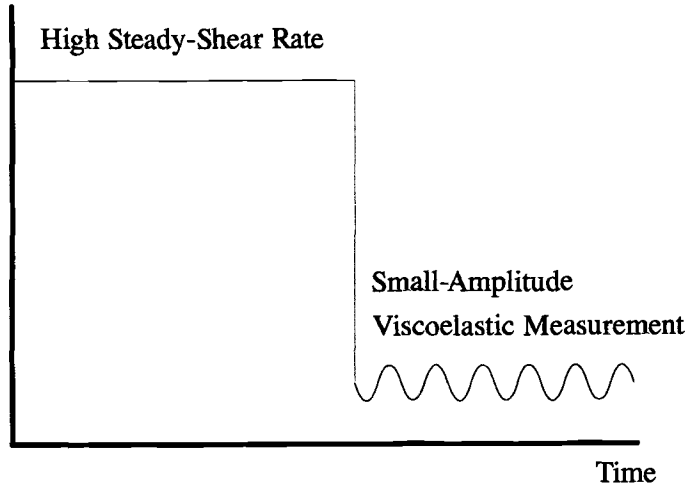

FIG. 10*a*—Viscoelastic characterization of structural recovery by step-shear method using small amplitude oscillatory strain for recovery phase.

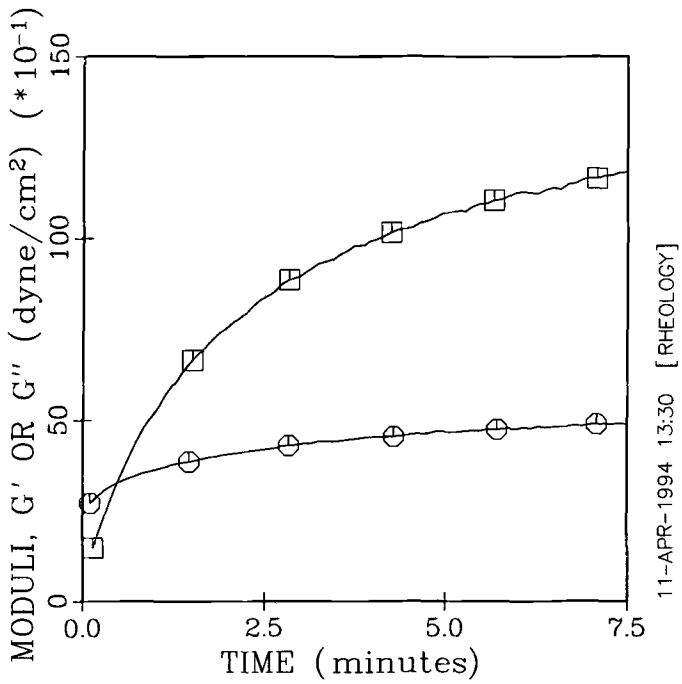

FIG. 10*b*—Experimental curves of *G'* (elastic modulus, □) and *G''* (viscous modulus, ○) versus time for a viscoelastic step-shear experiment.

Barnes and Walters [*29*] have claimed that most materials with an apparent yield stress will be found, in reality, to have a high but finite viscosity if measured at sufficiently low stresses. In practical terms, yield stress behavior can have important consequences for the processing, stability, and application of coatings. There is quite obviously some sort of flow discontinuity that occurs at low stresses, the magnitude of which is apparently related to the number and strength of interparticle attractive forces [*28,30*]. The yield stress is therefore an "engineering reality" [*31*] that must be taken into

account when formulating paints or dispersions. A yield stress may be desirable or undesirable depending on the process in question. Materials with a yield stress will often exhibit thixotropy and viscoelasticity as well.

Static Versus Dynamic Yield Stress

There are two types of yield stress which may be measured. The first is the static yield stress, measured by the startup of flow from nonflowing conditions. The second is the dynamic yield stress, which is the shear stress at which a presently fluid material suddenly turns solid (or exhibits a flow discontinuity). Experimental methods exist for measuring both [*32*], and the type which is relevant to the particular process in question should be the one measured. For example, for long-term suspension of solids or for start-up flow in pumps, the static yield stress is relevant. Postapplication leveling and sag behavior would be governed by dynamic yield stress characteristics, including the kinetics of structural recovery (see thixotropy in **Time-Dependent Fluids**). Some have used curve-fitting techniques to obtain a value for the yield stress by fitting a mathematical model for flow to a rheological flow curve. The Bingham, Herschel-Bulkley, and Casson models contain a yield stress term and have been commonly used to obtain a yield stress from measured flow behavior. Such methods are questionable, however, since one is attempting to infer a property of the solid state from behavior of the fluid [*25,33*].

Yield Stress Test Methods

Startup-of-flow methods include the use of penetrometer-type instruments such as a thermomechanical analyzer, where increasing force is applied to a standard probe. The yield stress is determined as the break point of a force-penetration curve [*34*].

In recent years, a new type of instrument known as a controlled-stress rheometer has become commercially available that is well-suited to measurement of yield stress and other properties of structured materials. For this instrument, the shear stress is the independent (or controlled) variable, while the dependent (or measured) variable is the shear rate. This allows an experiment to be done whereby the stress is gradually increased from zero or a very low value, registering zero shear rate (i.e., infinite viscosity) until the applied stress reaches the yield value, whereupon the viscosity becomes finite. The instrument reports this value as the measured yield stress. Another recent method employs a special vaned rotor to remedy problems of slip with yield-stress materials [*35–37*]. The vaned rotor consists of rectangular blades or vanes fixed to a rotating shaft. Advantages of this geometry are: (1) there is little disturbance of the sample when this type of probe is inserted, and (2) when the rotor turns, the material moves as a solid "cylinder." Thus, the shear surface is within the material itself, avoiding problems of wall slip.

Practical Aspects of Yield Behavior

Some of the practical consequences of yield behavior occur in the processing of, for example, pigment dispersions. Dispersions with high yield stresses may be difficult to dispense accurately or reproducibly via automatic metering systems. Pumps may actually refuse to move or may cavitate while attempting to pump such materials; solenoid valves may "freeze." Coatings with significant yield stresses may exhibit poor leveling [*2*] since, as the shear stress decreases during the course of the leveling process, the material effectively becomes immobile when the dynamic yield stress is reached.

On the other hand, a small yield stress can be of great value in inhibiting settling of particulate suspensions. One can easily calculate the shear stress exerted on the surrounding medium by a spherical particle falling under the influence of gravity

$$\tau = \frac{F_g}{A} = \frac{\text{Force of gravity on particle}}{\text{Surface area of particle}}$$

$$F_g = \frac{4}{3}\pi R^3(\rho_p - \rho_l)g; A = 4\pi R^2$$

$$\tau = \frac{R}{3}(\rho_p - \rho_l)g$$

where R is the particle radius, ρ_p the particle density, and ρ_l the liquid density.

For a titanium dioxide particle of radius 0.2 mm and density 4 g/cm^3, the shear stress due to gravity acting on the particle is about 0.2 dyne/cm^2. To prevent settling of such a particle, the surrounding medium need only resist with an opposing stress of greater than 0.2 dyne/cm^2. Even this, alas, is impossible for a Newtonian liquid, be it water or honey, since it will flow under all stresses no matter how slight (it is only a question of how slowly). A pigment particle will inevitably settle out of such a fluid, especially for viscosities of practical magnitudes. However, if the suspending medium possesses a yield stress equal to or greater than the particle shear stress, the particle "thinks" it is suspended in a solid and will be suspended indefinitely. This argument assumes more or less ideal yield behavior, which, as described above, may rarely be encountered. A medium with a measured yield stress of apparently sufficient magnitude may or may not permit the particle to settle over long periods of time due to the possibility of viscous flow below the apparent yield point. Therefore, to ensure adequate practical stability, one should build in a higher yield value than that calculated from the above.

Elastic Liquids (Viscoelasticity)

In ideal viscous flow, all energy input is converted either to heat or energy of motion. None is stored (i.e., none is converted into potential energy). Therefore, viscous flow results in irreversible deformation. Newtonian liquids show essentially ideal viscous (also called "inelastic") behavior over a wide range of deformation rate. For ideal elastic ("Hookean") substances, all the energy of deformation is stored, similar to a stretched rubber band. Consequently, elastic deformation is not permanent, but is in fact completely reversible. Real fluids can display elasticity, but mixed with viscous character, in varying degrees. Hence, the term *viscoelastic* is applied to such materials. Not all non-Newtonian fluids have significant elastic properties, but many do. The presence of significant elasticity in colloidal systems generally means there is a microscopic three-dimensional structure, or association network (microstructure), within the fluid. Elementary flow units are linked together in some fashion such that the struc-

tural relaxation time (see below) is measurably long. This structure, and particularly the destruction and rebuilding process that occurs during and after coating application, can have great consequences for application and film formation processes. An example of this is the influence of elasticity on leveling of an applied coating [*38*] (see also Massouda [*39*] and Glass [*40*]).

As the term implies, viscoelasticity refers to a material response which is a combination of viscous and elastic behavior. Viscous flow superimposed on elastic strain results in the "relaxation," or gradual disappearance, of stress within the strained object. This is manifested as an imperfect, or fading, stress memory. Figure 11 illustrates the material response to an applied elongational stress for a material with permanent stress memory (e.g., rubber band) and one with fading stress memory (e.g., "bouncing putty").

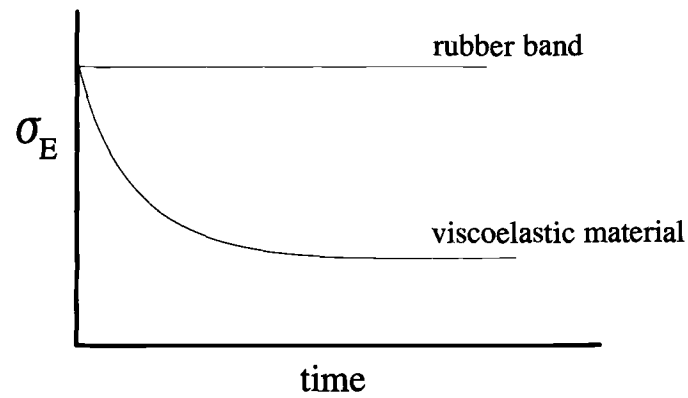

FIG. 11–Viscoelastic stress-memory loss: stretch-force experiment. Rubber band is cross-linked polymer, does not relax stress (σ_E) when stretched. Viscoelastic material can accommodate to strain by molecular motion (viscous flow), allowing elastic stress to decay.

The Viscoelastic Parameters and Their Measurement

A convenient way of experimental characterization of viscoelastic materials is by alternating the direction of strain (or stress). Most often, a sinusoidal deformation is employed (Fig. 12). The strain amplitude must be kept small so that the material response remains in the linear viscoelastic region where stress and strain are linearly related.[8] In perfectly elastic behavior (Hookean spring), the stress and strain are "in phase" with each other, that is, upon deformation, the maximum stress and maximum strain occur at the same instant in time. If there is any viscous (energy-loss) component in the material response, the stress and strain maxima will not be coincident, but will be "out of phase." This happens because viscous flow relieves the stress within the material, causing the stress maximum to occur before the strain maximum. That is, as the rate of strain decreases near the maximum (or minimum) of the strain sine wave, stress relaxation "catches up" and overtakes the stress-building effect of the strain. The separation in time of the stress and strain maxima is called the *phase shift* (or *phase angle*, the fraction of a complete cycle in degrees or radians that the phase shift represents). The phase shift is often given the symbol δ. The faster the viscous stress-relaxation process, the earlier in the cycle the stress maximum will occur, i.e., the larger the phase shift will be. The limiting value of the phase angle for purely viscous liquids is 90° (see Fig. 12). The reason is that, for sinusoidal deformation, the maximum strain rate (maximum slope of the strain sine wave) occurs 90° ahead of the maximum strain, and that, for Newtonian liquids, the stress is proportional to strain rate. Therefore, the maximum stress must occur at the maximum strain rate, which corresponds to a phase shift of 90°.

The derivation of viscoelastic parameters from a sinusoidal shear experiment begins with the calculation of the complex shear modulus, G^* (refer to Fig. 13). This is simply the ratio of the maximum stress, σ_0, to the maximum strain, γ_0 ($G^* = \sigma_0/\gamma_0$). From G^* may be separated G', the modulus of elasticity (storage modulus), and G'', the viscous modulus (loss modulus). Figure 13 demonstrates the geometric relationship of G^* to its in-phase and out-of-phase components, G' and G'', governed by the phase angle, δ. It is obvious from geometry

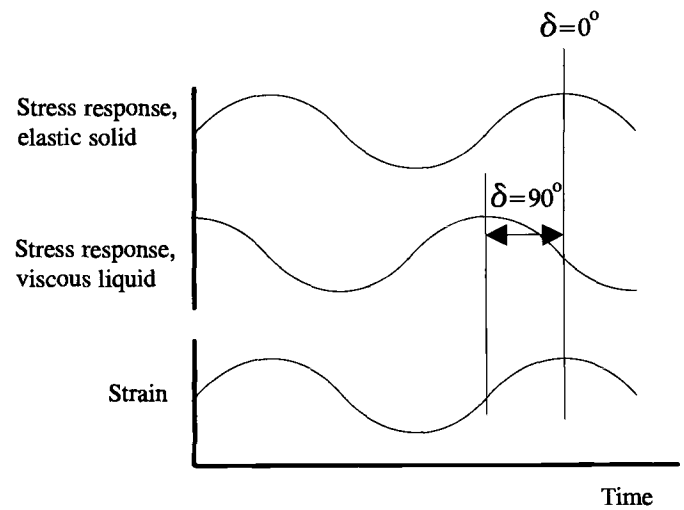

FIG. 12–Phase shift δ for ideal viscous and elastic bodies.

that when δ is zero, $G^* = G'$, and when $\delta = 90°$, $G^* = G''$. The physical meaning is that, when $\delta = 0$, all of the measured modulus is due to elastic effects, and when $\delta = 90°$, the modulus consists entirely of viscous effects. This follows from the discussion of the phase shift, above. By trigonometry, $G' = G^* \cos \delta$ and $G'' = G^* \sin \delta$. Alternately stated, G' is the component of the complex shear modulus which is in phase with the strain. G' therefore represents the elastic part of viscoelastic behavior. The viscous component (G''), on the other hand, is derived from the part of the modulus which is out of phase with the strain, but in phase with the strain rate.

Consider a dynamic test in which a sinusoidally varying strain is applied to a viscoelastic material. The angular frequency of the deformation is given by $\omega = 2\pi f$, where f is the frequency of oscillation (s^{-1}) and ω is in rad/s. Now, the amplitude of the strain with time is given by

$$\gamma = \gamma_0 \cos \omega t \tag{19}$$

which describes a cosine wave of maximum amplitude γ_0 and period $1/\omega$. The strain rate experienced by the material is then

$$\dot{\gamma} = -\omega\gamma_0 \sin \omega t \tag{20}$$

[8]This is a requirement because the equations used are valid only in the linear viscoelastic region.

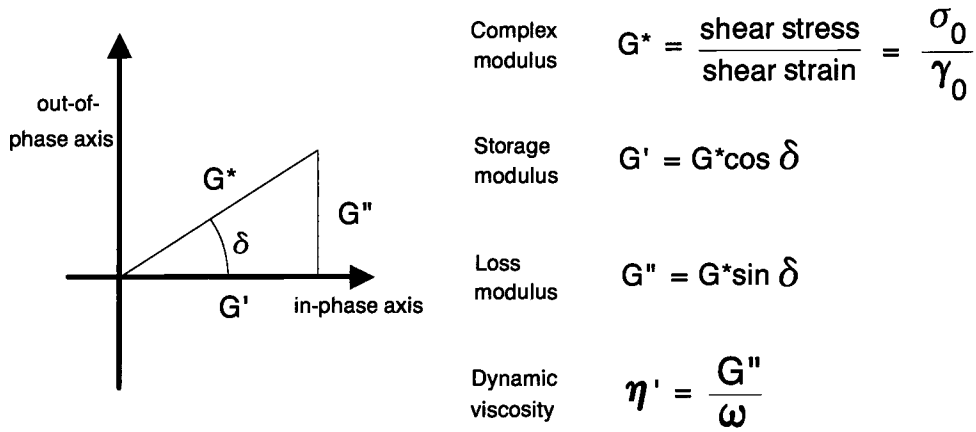

FIG. 13–Viscoelastic relationships in the complex plane.

The oscillating strain produces a stress response

$$\sigma = \sigma_0 \cos(\omega t + \delta) \tag{21}$$

where δ is the phase shift, advancing the phase of the stress relative to the strain. Equation 21 may be equivalently written [*96*]

$$\sigma^* = \sigma_0 \cos\delta \cos\omega t - \sigma_0 \sin\delta \sin\omega t \tag{22}$$

which describes a complex stress, where, by complex plane relationships analogous to Fig. 13, $\sigma_0 \cos\delta$ is the stress component in-phase with strain and $\sigma_0 \sin\delta$ the stress component which is out-of-phase with the strain (but in-phase with the strain rate). We therefore can define a dynamic viscosity, η', as the quotient of the stress in-phase with the strain rate divided by the strain rate

$$\eta' = \frac{\sigma_0 \sin\delta}{\dot{\gamma}_0} = \frac{\sigma_0 \sin\delta}{\gamma_0\omega} = \frac{G^* \sin\delta}{\omega} = \frac{G''}{\omega} \tag{23}$$

The above expression is obtained using the relationships $\dot{\gamma}_0$ (strain-rate amplitude) $= \gamma_0\omega$ and $G^* = \sigma_0/\gamma_0$.

The magnitudes of G'' and G' reveal the relative importance of viscous and elastic behavior in the mechanical response of a material. In Fig. 13, again by trigonometry, the tangent of the phase angle equals the ratio G''/G'. Thus, tan δ quantifies the balance of energy loss to energy storage measured under certain conditions of temperature, pressure, and frequency or rate of deformation. For solids, tan δ can be useful to predict the likelihood of brittle or ductile failure of a polymer or the sound absorption or vibration damping properties. For liquids, tan δ can monitor the progress of fluid restructuring in thixotropic recovery. The latter may be useful in computing sag resistance for when tan δ becomes less than unity, the system has essentially become immobolized (i.e., reached a "dynamic yield point"). When tan $\delta > 1$, viscous flow (i.e., a steady-state viscosity) is possible. When tan $\delta < 1$, however, the material is more elastic than viscous (i.e., a percolating network extends throughout the bulk, and it is essentially an elastic solid).

Viscoelastic Models

It turns out that viscoelasticity can be rather realistically modeled by simple mechanical analogues. These are useful not only as an aid to conceptualization of viscoelastic behavior, but also in helping to understand the elementary mathematics of viscoelasticity. As we have said, viscoelasticity is a combination of two idealized behaviors: Hookean elasticity and Newtonian viscosity. The mechanical analogue of Hookean behavior is a spring of force constant G, and that of Newtonian flow is a "dashpot" (a piston-in-cylinder filled with a viscous fluid of viscosity η). These elements are combined in various ways to model viscoelastic mechanical response.

To build our first model, we will connect a spring and dashpot in series (Fig. 14), an arrangement known as the Maxwell model. To imagine what response the model has, let's apply a constant stress, σ_0, to one end, the other being fixed. By the way, our dashpot is considered to be infinitely long so that the piston never runs out of travel. This being the case, one can see that an equilibrium strain would never be reached, but the dashpot would continually move as long as the stress is applied. Since the model can "flow" without limit, this is obviously a model for viscoelastic liquids (sometimes called "elasticoviscous"). We have just described what is known as a creep experiment, in which a sudden stress σ_0 is applied, and the evolution of strain, or deformation, is followed with time. The creep of a Maxwell liquid is not very interesting, however. The strain-time curve consists merely of a straight line with intercept equal to σ_0/G and slope of σ_0/η (Eq 26).

We will use the Maxwell model to illustrate how equations describing viscoelastic behavior may be derived. Just as the stress is the same in every part of a stretched string, so is the stress the same on both elements for the Maxwell model, and also, therefore, the rate of change of stress is identical as well.

$$\sigma_{\text{Total}} = \sigma_{\text{Elastic}} = \sigma_{\text{Viscous}} (= \sigma_0) \tag{24}$$

and

$$\dot{\sigma}_T = \dot{\sigma}_E = \dot{\sigma}_V \tag{25}$$

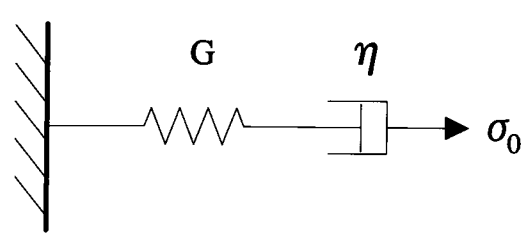

FIG. 14–Maxwell model. *G* is force constant of spring; η the viscosity of dashpot fluid; σ_0 is the applied stress.

Furthermore, the total strain is clearly the sum of the strains undergone by the two elements

$$\gamma_T = \gamma_E + \gamma_V = \frac{\sigma_E}{G} + \frac{\sigma_V t}{\eta} \tag{26}$$

The expression on the right follows from the definition of the modulus ($G = \sigma/\gamma$), Eq 4, and the fact that $\gamma = \dot{\gamma}t$. It is also true that

$$\dot{\gamma}_T = \dot{\gamma}_E + \dot{\gamma}_V = \frac{\dot{\sigma}_E}{G} + \frac{\sigma_V}{\eta} \tag{27}$$

An alternative to the creep method that is particularly useful for viscoelastic solids is to apply a sudden deformation and follow the decay of stress with time. This is similar to the experiment depicted in Fig. 11 and is known as *stress relaxation.* Sudden imposition of a strain γ_0 results in instantaneous lengthening of the spring. The dashpot experiences, in turn, an initial stress σ_0 from the extended spring, causing a gradual movement of the dashpot's piston, resulting in relaxation of the stress. By manipulation of the above equations, we can arrive at a quantitative way of describing this relaxation process.

Since the strain in a stress-relaxation experiment is constant (γ_0), the total strain rate, $\dot{\gamma}_T = 0$. Therefore, from Eq 27

$$\frac{\sigma_V}{\eta} = -\frac{\dot{\sigma}_E}{G} = -\frac{d\sigma/dt}{G} \tag{28}$$

rearranging

$$\frac{d\sigma}{\sigma_V} = -\frac{G}{\eta}dt \tag{29}$$

Integrating Eq 29 from time 0 to time t results in the Maxwell stress relaxation expression

$$\sigma = \sigma_0 e^{-Gt/\eta} \tag{30}$$

Figure 15 illustrates the decay of stress in a constant strain or stress relaxation experiment for the Maxwell model, described by Eq 30. Note that the quantity η/G has the dimension of time. We will assign to this quantity the symbol λ and refer to λ as the stress-relaxation time constant. It can be seen from Eq 30 that when $t = \eta/G$, $\sigma = \sigma_0/e$. Therefore, λ represents the time required for the stress to fall to $1/e$ of its initial value (Fig. 15) and gives a convenient way of quantifying the rate of decay of stress in viscoelastic materials.

The time constant, λ, could also be called the stress memory time constant since it is related to the time it takes for a viscoelastic material to "forget" its initial elastic stress level when subjected to a constant strain. As such, λ determines the role that viscoelasticity plays in an industrial process. That is, elastic materials generate an "extra (elastic) stress" when deformed, which may result, for example, in the stabilization of fluid structures which would ordinarily collapse too quickly to be important. These include, for example, liquid fibers and webs, which result in roller spatter [*41*]. The magnitude of the undesirable effect will depend on the rate at which the elastic extra stress decays or "relaxes," as we'll see below.

In modern rheometers, sinusoidal oscillation is the most common method of viscoelastic characterization. (Creep is also available as a viscoelastic test mode for controlled-stress instruments and stress relaxation for controlled-rate instruments—see below.) Equations derived for the Maxwell model [*42,43*] show how the viscoelastic time constant, λ, may be obtained from the oscillatory data

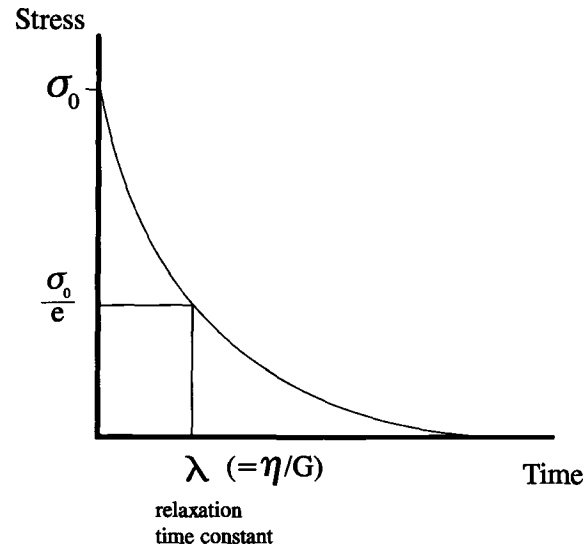

FIG. 15–Stress relaxation (constant strain) experiment. Initial elastic stress σ_0 relaxes viscously with a time constant λ (= η/G). λ corresponds to the point where stress has fallen to a value σ_0/e.

$$\eta'\omega = G'' = \frac{G_\infty \omega\lambda}{1 + \omega^2\lambda^2} \tag{31}$$

and

$$G' = \frac{G_\infty \omega^2\lambda^2}{1 + \omega^2\lambda^2} \tag{32}$$

from which

$$\tan\delta = \frac{G''}{G'} = \frac{1}{\omega\lambda} \tag{33}$$

where G_∞ is the plateau modulus (limiting value of G' reached at high frequency = Maxwell spring constant). Equation 33 says that when G' and G'' cross over ($\tan\delta = 1$), $\lambda = 1/\omega_c$ (ω_c is the crossover frequency). The plateau modulus can be obtained from Eq 32, as well, since at the crossover point $G_\infty = 2G'$. Similarly, at crossover, the zero-frequency plateau viscosity, $\eta_0 = 2\eta'$ (from Eq 31).

If the mechanical elements are connected in parallel rather than series, they each experience identical strain, but the stresses are now additive. This arrangement is called the Kelvin-Voigt model (Fig. 16). Because the elements are now in parallel, the Kelvin-Voigt model can only undergo finite strain, limited by the extensibility of the spring. Therefore, this is a model for a viscoelastic solid below its yield point. Equations for creep, stress relaxation, and $\tan\delta$ for the Kelvin-Voigt model are

Kelvin-Voigt creep

$$\gamma = \frac{\sigma_0}{G}(1 - e^{-t/\lambda}) \tag{34}$$

Kelvin-Voigt stress relaxation

$$\sigma = \gamma_0 G \tag{35}$$

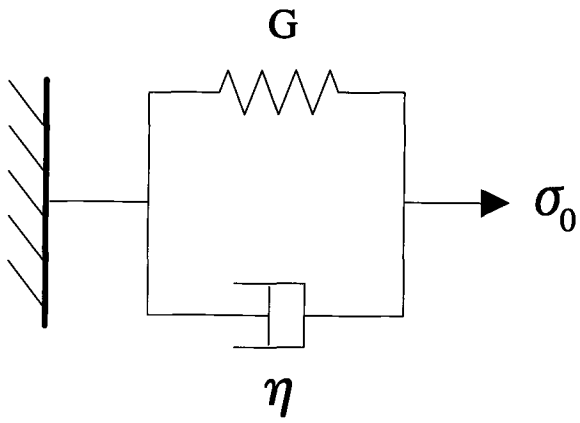

FIG. 16–Kelvin-Voigt model. Symbol definitions same as Fig. 14.

$$\tan \delta = \omega\lambda \tag{36}$$

These equations describe an exponentially increasing strain at constant stress (see Fig. 17 and Eq 34) and a nonrelaxing stress at constant strain (Eq 35), respectively.

The Maxwell and Voigt models, by themselves, are too simple to describe accurately most real viscoelastic materials. However, a Maxwell element connected in series with a Kelvin-Voigt element turns out to model the linear viscoelasticity of many real systems rather well. Figure 18 shows such an arrangement, known as the Burgers model. For completeness (and also because an error in the Burgers stress-relaxation expression has crept into the literature), equations describing creep and stress relaxation behavior for the Burgers model are given

Burgers creep

$$\gamma = \frac{\sigma_0}{G_2} + \frac{\sigma_0 t}{\eta_2} + \frac{\sigma_0}{G_1}(1 - e^{-t/\lambda_1}) \tag{37}$$

Burgers stress relaxation

$$\sigma = \gamma_0 G_2 e^{-t/\lambda_2} + \gamma_0 G_1 \tag{38}$$

where $\lambda_1 = \eta_1/G_1$ and $\lambda_2 = \eta_2/G_2$. The creep and stress relaxation behavior for the Burgers model are shown in Figs. 19 and 20. Modern rheometers of the type known as "controlled stress" (see **Rotational Instruments**) are capable of performing creep measurements. Viscoelastic constants can

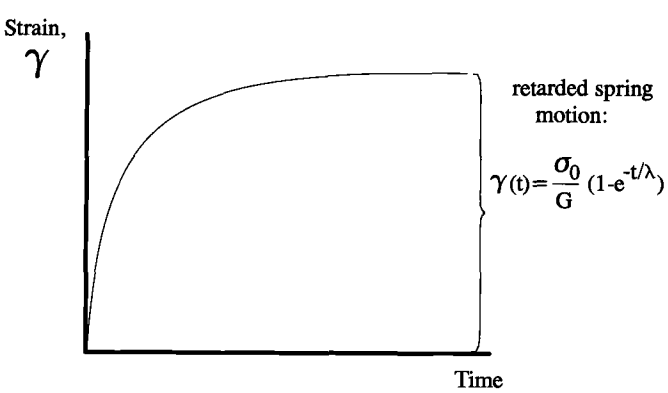

FIG. 17–Kelvin-Voigt creep (constant stress) experiment. At constant applied stress σ_0, strain increases exponentially with time constant λ (= η/G).

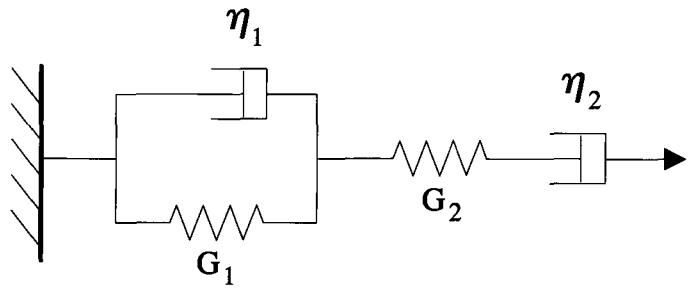

FIG. 18–Burgers model. Symbol definitions same as Fig. 13. Subscript 1 refers to the Voigt element, 2 to the Maxwell element.

then be extracted from the data by analysis according to one or more of the above models.

Viscoelasticity and Industrial Processes

Now, since industrial processes are of many types, how do we assess the effect of elasticity on a given process? That depends in part on the length of time the process stress is applied to the material. That is, what's most important is not how rapidly a stress is applied nor even the magnitude of the stress, but for how long the stress is applied relative to the time required for any elastic "extra" stress to decay. This suggests taking a ratio of the stress relaxation time, λ, to the time (duration) of the process stress, t

$$De = \frac{\lambda}{t} \tag{39}$$

This ratio is a defined rheological term known as the Deborah number, *De*. It is named for the Biblical prophetess Deborah, who prophesied that the "mountains flow before the Lord" [*44*]. This is a perfectly accurate statement, made long before being verified by the science of geology, of the fact that, on God's time scale, rock formations can be observed to undergo permanent deformation, or flow. In other words, if the stress time scale, t, greatly exceeds the relaxation time, λ ($De \ll 1$), the material will respond as a viscous fluid (because elastic stress has time to decay). Conversely, if $De \gg 1$, the stress duration is too brief to provide an opportunity for viscous relaxation, and the material behaves as if an elastic solid. Thus, the Deborah number quantifies the proportion of elastic to viscous control of a process. This is one reason why a determination of the viscoelastic properties of paints and coatings is important. The results of an analysis by Keunings [*38*] of the effect of viscoelasticity on leveling can be adapted to the situation of a typical paint, and the influence of the elastic-stress relaxation time constant on leveling rate is shown in Table 4. To be sure, real materials may not exhibit simple exponential stress decay (i.e., a single relaxation time), but rather may possess a spectrum of relaxation times. However, the mechanical response will be dominated by a "mean" relaxation time (or sometimes the longest relaxation time [*38*]), obtained from experiments such as described in foregoing sections. Simple viscoelastic dispersions can show Maxwellian behavior with a single relaxation time [*45,46*].

One of the reasons that associative thickeners (ATs) have been so successful in being able to thicken paints without at the same time adversely affecting flow and leveling is no doubt due in part to their low elasticity. Even though ATs

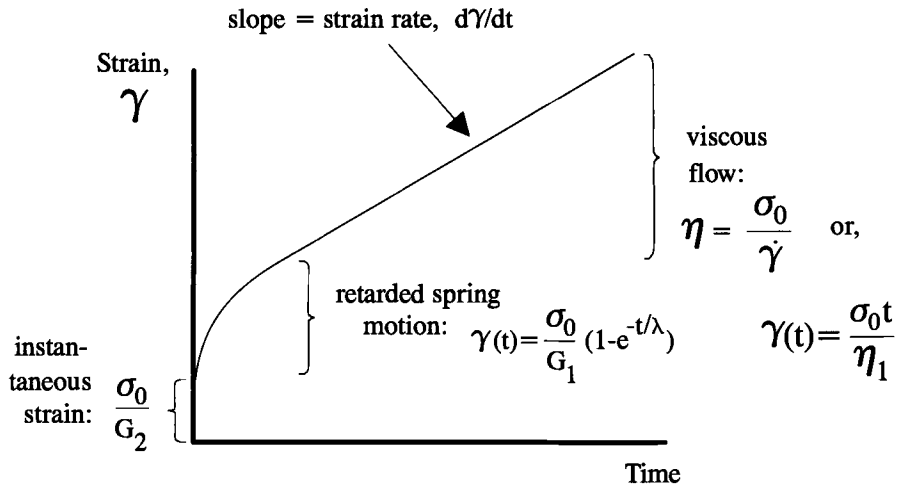

FIG. 19–Burgers creep (constant stress) experiment. Under applied stress σ_0, the Burgers model undergoes instantaneous deformation equal in magnitude to σ_0/G. In next segment of curve ("retarded spring motion") strain increases exponentially with time. Finally, spring is fully extended and viscous flow occurs with a constant strain rate.

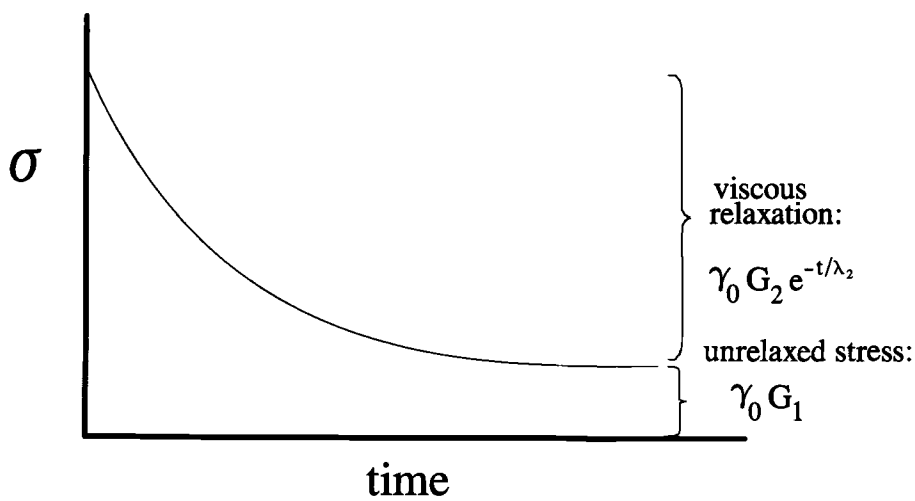

FIG. 20–Burgers model stress relaxation (constant strain). Stress generated by initial strain γ_0 decays exponentially governed by the relaxation time λ_2 (= η_2/G_2). Voigt element contributes unrelaxed stress $\sigma_\infty = \gamma_0 G_1$.

TABLE 4—Leveling rate dependence on Maxwell relaxation time, λ. $\alpha = da/dt$, where a = roughness amplitude, and $t_{1/2}$ = time for $a \rightarrow 0.5a_0$ (initial amplitude).

λ, s	0.0	0.1	1.0	10.0	50.0	100.0
α, s^{-1}	34.5	7.75	0.972	0.0997	0.02	0.01
$t_{1/2}$	0.020	0.09	0.67	6.95	34.7	69.3

generate a three-dimensional network structure within the fluid,[9] they typically would have negligible G' values, in contrast to typical cellulosic thickeners, for example. This is believed to be due to the extreme lability of the micellar junctions of the associative network, resulting in very short network relaxation times [*46,47*]. Thus, the decay of elastic stress in ATs is so rapid that such stresses are virtually unobserved ($De \ll 1$).

[9]See Chapter 30—Thickeners and rheology modifiers.

As stated before, the process consequences of viscoelasticity stem partly from the stabilization of otherwise unstable liquid structures by the elastic "extra stress." Thus, liquid fibers and "webs" which would ordinarily collapse by surface tension are stabilized, producing, for example, excessive rollcoat spatter (or "misting") and ribbing, and inhibiting atomization of sprayed materials. The importance of viscoelasticity for a particular process is gauged, using the Deborah number, by the ratio of the stress-relaxation time constant to the time duration of the process stress. Of course, both the magnitude and lifetime of the elastic stress will be important, for together they will govern the degree of stabilization.

The analysis of the problem is complicated by the fact that many processes, particularly of coatings application, involve strain magnitudes outside the range of linear viscoelasticity. Approaches to nonlinear viscoelasticity exist, but are beyond the scope of this chapter. Quantitative prediction of viscoelas-

tic effects would require the use of a model for the fluid behavior, or viscoelastic constitutive equation, also outside the scope of this presentation. However, it is often possible to build experimental correlations between coating elasticity and performance problems, so that guidance may be provided for formulation efforts to solve them.

For most modern coatings, in particular, the origin of elasticity is likely to be an associated structure built up from a dispersed phase rather than polymeric entanglement. Such particulate flocs are generally shear-sensitive and are reduced or destroyed by high-shear application processes. The elastic modulus G' will be seen to decrease with increasing strain and strain rate outside the linear regime. Thus, in most cases, G' is a measure of structure that has its greatest effect at low strain and strain rate (unless the elastic character is high-polymeric in origin). Therefore, under most conditions of application, structure (therefore elasticity) is destroyed and must rebuild in the applied film. Herein, it is seen that thixotropy and viscoelasticity are kindred phenomena.

EXTENSIONAL RHEOLOGY

The other important deformation occurring in coatings besides simple shear is extensional (or elongational) deformation. Extensional or "stretching" deformation causes an increase in length and decrease in cross section of an object. In a simple shear field, particles or polymer coils (i.e., the flow units) rotate with a velocity $\dot{\gamma}/2$. The rotational motion lessens the friction between the solvent and solute particles. In an extensional flow, this rotational accommodation to the flow field is not possible because there is no velocity gradient normal to the flow direction. The separation of flow units is thus more costly in terms of energy dissipation due to friction. Thus, the viscosity of a Newtonian fluid in extension turns out to be three times greater than its viscosity measured in shear (Trouton rule).

The extensional viscosity (η_e) is calculated as the ratio of tensile stress to extensional deformation rate

$$\eta_e = \frac{\sigma_e}{\dot{\epsilon}} \tag{40}$$

The strain in extension is usually defined as a Hencky strain, $\epsilon = \Delta l/l_0$, where l_0 is the original length and Δl the increase in length under tensile stress σ_e. The Hencky strain rate is then the time derivative of the strain or

$$\dot{\epsilon} = \frac{1}{l}\frac{dl}{dt} = \frac{d(\ln l)}{dt} \tag{41}$$

Extensional Viscosity in Coatings Processes

Many coatings processes involve stretching (elongational) flows (Table 1), and when coatings can support large extensional stresses (i.e., high extensional viscosity) performance can be dominated by such flows. As mentioned, the viscosity of a Newtonian liquid in extension is three times that measured in shear. For non-Newtonian fluids, the Trouton ratio $[\eta(\dot{\epsilon})/\eta(\dot{\gamma})]$ can be as much as 10^4. Furthermore, whereas the shear viscosity is usually a decreasing function of shear rate, extensional viscosity frequently displays strong extensional strain rate thickening. For example, Lu [*48*] observed that polyacrylamide thickeners in latex paint systems showed extensional thickening behavior, whereas hydroxyethylcellulose-type thickeners did not. Coatings application processes are generally high strain rate, so it is clear that η_e can dominate the mechanical response, generally leading to detrimental consequences. Extensional stresses can stabilize liquid "webs" and fibers, such as form in direct rollcoating, allowing them to grow large instead of dissipating. This can result in heavy ribbing and "misting" (roll spatter) [*49*]. On the other hand, the breakup of a liquid jet to form atomized droplets in spray application is suppressed by a high extensional viscosity because the liquid fibers formed intermediary to droplet formation are inhibited from disintegration. J. E. Glass has been the chief proponent of the study of extensional viscosity in relation to paint performance, correlating it to roller spatter [*41*] and the performance of sprayed coatings [*50*]. Massouda did a clever and, unfortunately overlooked study of the relationship of extensional stress measurements to viscoelastic relaxation kinetics and thence to spattering of paints [*39*].

Extensional Viscosity Measurement

There are, unfortunately, few commercial instruments suitable for extensional measurement on coatings. Carri-Med (division of TA Instruments) markets the Spin-Line Rheometer (SLR) utilizing the fiber-spinning geometry. Rheometrics' RFX rheometer is probably better suited to low-viscosity fluids, using opposed-nozzle flow to measure extensional forces (the latter instrument offers dual high-shear and extensional measurement capability). With the necessary electromechanical design and fabrication resources, one might attempt to build a simple extensional rheometer, perhaps patterned after that of Gupta [*51*]. The relatively simple technique of convergent flow analysis was used by Lu for measuring extensional properties of latex paints [*48*]. An overview of extensional rheometry has recently been published by James and Walters [*52*].

POLYMER MELT AND SOLUTION RHEOLOGY

High-polymer solution rheology is a subject of relatively little interest with respect to coatings due to the shift from solvent-borne to environmentally compliant technologies, such as water-borne, higher solids, and powder coatings. The polymers used for high solids and powder coatings are little more than oligomers in order to achieve necessary flow for satisfactory processing and film formation. Even the modest molecular weight polymers used in solvent-borne varnishes and paints are below the entanglement molecular weight, M_c, hence, both their neat and solution rheology are Newtonian. Similarly, powder coating melts are Newtonian until near gelation [*53*]. The viscosity of polymer solutions below M_c is proportional to the weight-average molecular weight, M_w,

$$\eta_0 = KM_w (M_w < M_c) \tag{42}$$

where K is a constant dependent on chain flexibility (T_g), polymer-solvent interaction, temperature, etc. If $M_w > M_c$,

the motion of entangling polymers becomes much more complex, and the viscosity now depends on M_w raised to the power of approximately 3.4 [54].

$$\eta_0 = KM_w^{3.4} (M_w > M_c) \tag{43}$$

The viscosity of polymer melts follows a similar relationship. It should be noted that polymers having highly polar or hydrogen-bonding functionalities (such as commonly used in high-solids formulations) can show nonlinear dependence of viscosity on molecular weight even below M_c due to transient intermolecular associations [55].

The sole use of high-polymer binders in coatings today is where they exist as a separate phase dispersed in a liquid carrier medium.[10] Such materials are known as polymer latexes, or latex dispersions. Because the latex polymer is segregated from, and therefore noninteracting with, the solvent, the rheology of latexes is much simpler than that of the same high polymer in the solution state. The rheology of polymer dispersions will be discussed below.

DISPERSION RHEOLOGY

A dispersion (or suspension) consists of a suspended or dispersed discontinuous phase contained in a continuous phase. As an example, for coatings in particular, this might be a system in which a fine particle size solid is wetted by and thoroughly mixed in a liquid. However, the dispersed phase may be a liquid or semisolid (or gaseous) as well. The dividing line between dispersions and suspensions is essentially one of particle size. Dispersions are generally of colloidal dimension, about 10 nm to 1 μm. Due to their small size and mass, colloidal particles are very slow settling or nonsettling because Brownian motion effectively keeps them randomly suspended. Suspensions range in size above 1 μm and generally exhibit rapid settling because Brownian forces are ineffective with such massive particles, and also because Van der Waals attractive forces increase in proportion to particle size.

Addition of a particulate phase to a liquid modifies its viscosity and sometimes its rheology. The modification to the continuous-phase viscosity made by an added particulate phase depends on characteristics of the particle and on the particle concentration. The contribution of a single particle to the viscosity of a dispersion is characterized by its intrinsic viscosity (or limiting viscosity number), $[\eta]$. The primary factors governing $[\eta]$ are particle shape and deformability. The influence of particle concentration on viscosity is expressed by the volume fraction (or internal phase volume) ϕ, the fraction of the total volume of the suspension occupied by the suspended material and which is a dimensionless number. A convenient way of expressing the effect of a dispersed phase on the viscosity of a liquid is by normalizing the dispersion viscosity to the pure-liquid viscosity. This ratio is termed the relative viscosity η_r and is also dimensionless.

$$\eta_r = \frac{\eta_d}{\eta_l} \tag{44}$$

[10]Some high-molecular-weight, water-soluble polymers are used as thickeners. However, they are used at low levels, and their effects on rheology are mainly colloidal/osmotic rather than as solution polymers.

It is reasonable that the viscosity of a liquid will be augmented by a factor equal to the product of the particle intrinsic viscosity and the concentration of particles.

$$\eta_r = 1 + [\eta]\phi \tag{45}$$

Einstein [56] was the first to calculate the intrinsic viscosity for noninteracting rigid spheres in a Newtonian liquid and obtained the number 2.5

$$\eta_r = 1 + 2.5\phi \tag{46}$$

The intrinsic viscosities of other particle shapes (e.g., prolate and oblate spheroids—discs and rods) have been calculated [57] and are always greater than 2.5. This means that any deviation from spherical particle shape will increase dispersion viscosity. Equation 46 is valid only in the very dilute regime ($\phi < 0.05$). Batchelor [58] extended the rigorous treatment to somewhat higher volume fractions by using a second-order expression in ϕ

$$\eta_r = 1 + 2.5\phi + k\phi^2 \tag{47}$$

The value of k ranges from 5.2 to 6.2. Figure 21 illustrates the typical dependence of η_r on ϕ for actual dispersions (using data of Eilers [59]) and shows curves corresponding to the predictions of Einstein's and Batchelor's equations. It can be seen that Batchelor's equation predicts a finite viscosity at $\phi = 1$, which is not realistic. Also in Fig. 21, it is seen that η_r rises toward infinity at a volume fraction considerably smaller than unity. The volume fraction corresponding to $\eta_r \rightarrow \infty$ is denoted ϕ_m, the maximum volume fraction, or maximum packing fraction. At $\phi = \phi_m$, the density of particle packing is such that the dispersion can no longer flow. The value of ϕ_m will be system-dependent and will be determined by particle shape, particle-size distribution, the ionic strength of the medium, the degree of particle flocculation, and the exact manner in which the particles arrange themselves (pack) in three-dimensional space.

Numerous models have been proposed to take account of the limiting concentration parameter ϕ_m [15,59–61]. Probably the model which has been most successful in fitting a variety of data is the Krieger-Dougherty equation [62]

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \tag{48}$$

Figure 21 shows the fit of the Krieger-Dougherty model to some data of Eilers [59] with a value of $[\eta]$ close to the Einstein value. The maximum packing fraction will, in fact, have different, unique values at low and high shear rates because the strength of the shear field determines the way particles pack together. Recent reviews of the rheology of polymer colloids are recommended for further reading [6,14].

It should be noted here that, although the dispersion rheology is controlled by the disperse-phase volume fraction, ϕ, the effect of the particle phase on the rheology may be greater than expected on the basis of the volume of material added to make up the dispersion. This is because the disperse-phase volume may be augmented by various effects tending to increase the effective particle radius. It is the "hydrodynamically effective" particle volume that determines the rheology. Thus, the rheological behavior will be found to scale with the "effective" volume fraction, ϕ_e, rather than with

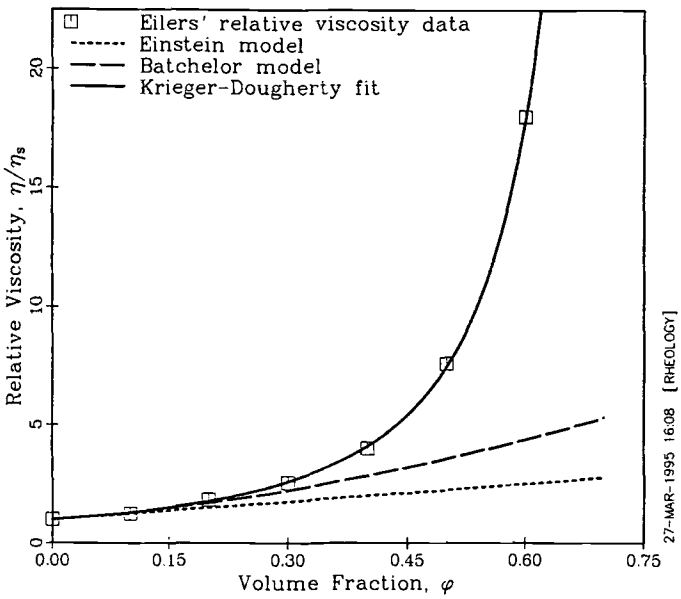

FIG. 21–Relative dispersion viscosity data of Eilers, together with best-fit curves for the Einstein model, Batchelor model, and the Krieger-Dougherty model.

the formulated volume fraction, ϕ. The effective particle radius can be increased in a number of ways, often as a consequence of employing various methods of achieving stabilization of dispersions. Adsorption of a polymeric stabilizer onto the surface of a particle adds the thickness of the stabilizer layer to the particle radius. This layer prevents the close approach and flocculation of particles by steric interactions between stabilizer layers, resulting in steric stabilization. If the thickness of the steric stabilizing layer on the particle is δ, the effective volume fraction is [*63*]

$$\phi_e = \phi\left[1 + \left(\frac{\delta}{R}\right)^3\right] \tag{49}$$

where R is the original particle radius. Quantitative viscometric methods have been developed for inferring the adsorbed-layer thickness [*63,64*].

Aqueous dispersions are often stabilized by association of repulsive electrical charge with the particle, known as electrostatic stabilization. The charge may be due to adsorption of ions, anionic or cationic surfactants or polyelectrolytes, or, in the case of polymer colloids, to the presence of ionizable groups which are part of the polymer molecules. (In the case of functionalized polymer latexes, such groups tend to migrate to the particle surface.) The surface ionic charge propagates an electrical potential field into the aqueous phase, depending on the ionic strength of the medium. In the presence of dissolved counterions, an ionic "atmosphere" develops around the charged particle. These phenomena are the origin of the so-called electroviscous effects, which have to do with the way the electrical field surrounding the particle affects the effective volume fraction or collision cross section, and the nature of the hydrodynamic interaction between particle and surrounding liquid [*57,65*]. Dispersion rheology can be greatly altered as a consequence of these effects, as the solution ion concentration or pH are varied. Krieger and Eguiluz showed the η_r of a dispersion of uniform polystyrene latex spheres (ϕ = 0.4) decreased from 10^6 to 10 for a two-orders-of-magnitude increase in concentration of electrolyte [*66*]. In that study, the low-electrolyte latexes exhibited apparent yield stress behavior, a consequence of the increase of the effective volume fraction of the latex particles due to the expansion of the repulsive electrostatic field. The effect is so great that the particles are actually "locked" into crystalline arrays that can diffract light, producing striking iridescent colors. As the electrolyte concentration is increased, the counterion "cloud" both shrinks the electrostatic field and shields particle fields from each other. Consequently, the viscosity drops dramatically (remember that the volume change depends on the cube of the radius change).

Rheology is particularly useful for dispersion characterization because of its sensitivity to microstructure. Dispersion rheology has two broad aspects: (1) the dependence of viscosity on the concentration of the dispersed phase, and (2) the dependence of viscosity on shear stress and shear rate, discussed in **CLASSES OF NON-NEWTONIAN BEHAVIOR.** To the foregoing are added effects of particle shape, rigidity, particle size and particle size distribution, and interparticle forces, both attractive and repulsive. All these factors combine to determine the microstructure of the dispersion and hence its rheology.

Dispersions can exhibit the full range of rheological behavior mentioned previously, including Newtonian, shear-dependent, time-dependent, plastic, and elastic behavior. A dispersion of noninteracting spherical particles will be Newtonian up to about ϕ = 0.2 [*15*]. Above this point, onset of non-Newtonian character begins due to particle interactions and hydrodynamic factors. Mechanisms for these effects are discussed in the section entitled **Shear-Thinning Fluids.**

SAGGING

A coating layer on any but a horizontal surface will experience a tangential shear stress due to gravity of magnitude

$$\tau = \rho g h \cos\theta \tag{50}$$

where ρ is the liquid density, g the gravitational acceleration, and h the uniform layer depth. θ is the angle of inclination of the substrate to the vertical. For a vertical substrate, $\tau = \rho g h$ (Fig. 22).

The shear stress on any layer within a coating will be equal to the load from the outer layers. For a vertical surface

$$\tau = \rho g(h - y) \tag{51}$$

is the shear stress acting on a layer a distance y from the substrate due to the weight of the outer layer of thickness $h - y$ (Fig. 22).

Coating layers having a yield stress τ_0 (see **Plastic (Yield) Behavior**) will not sag unless the gravitational shear stress exceeds the yield value. The shear plane where yield occurs will therefore be at y' (for ideal yield behavior) when the following expression is satisfied

$$\tau_0 \leq \rho g(h - y') \tag{52}$$

Since only layers deeper than y' experience sufficient stress to flow, it follows that the layer $h - y'$ (from y' to the free surface) is solid and slides as a solid sheet over the flowing

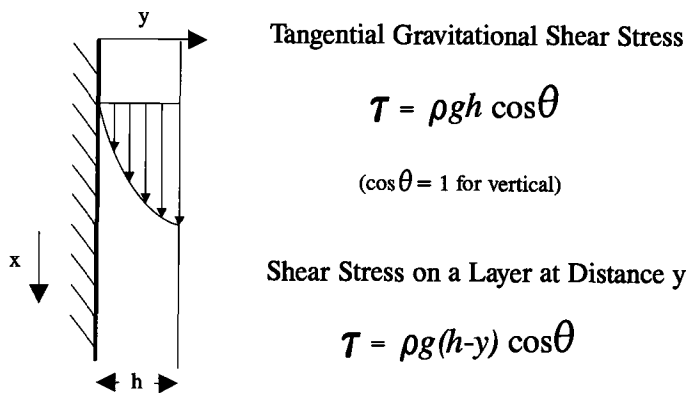

FIG. 22–Sagging, driven by gravitational shear stress.

inner layers. For a coating with a large yield stress, the load necessary to cause yield and flow is greater. Therefore, the yield plane moves deeper into the coating layer, leading to a phenomenon known as slumping. Slumping, therefore, is diagnostic of the presence of a significant yield stress. Figure 23 illustrates the effect of a yield stress on sagging, leading to plug flow (slumping). Croll [*67*] showed direct evidence of plug flow in a sagging coating possessing a yield stress.

The surface velocity of a sagging Newtonian liquid is

$$v = \frac{\rho g h^2}{2\eta} \tag{53}$$

(Wu [*68*] gives sagging velocity expressions for various non-Newtonian rheologies.) Sagging transmits substrate imperfections to the surface and amplifies them [*69*]. This is because any surface irregularity causes fluctuations in the effective local coating thickness normal to gravity and therefore in the local sagging shear stress. Furthermore, any local variations in film thickness due to application or to substrate features (e.g., a hole or a corner) can produce local accelerations of sagging in which thicker elements overtake thinner elements. This is a self-accelerating process, leading to drips, "tears," runs, or "curtaining" [*70*]. Such undesired flows can be minimized by proper characterization and control of rheology [*71*].

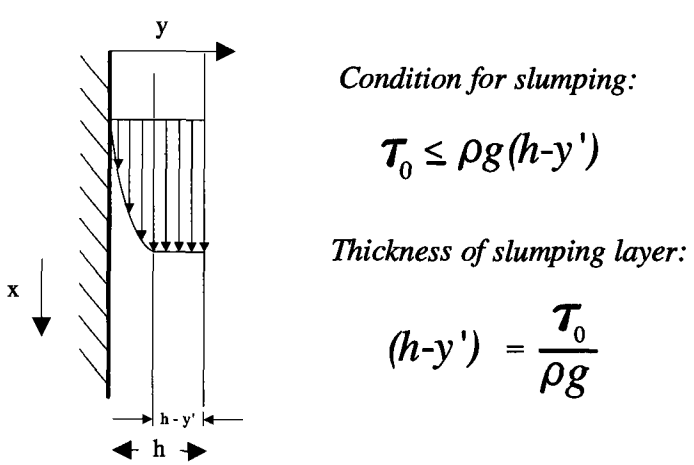

FIG. 23–Slumping (plug flow), caused by the presence of a yield stress, τ_0.

The sagging of a coating is similar to the problem of drainage of a liquid layer from an inclined surface. The difference between the two is that, in sagging, the coating layer is assumed infinite in extent; hence, sagging causes no change in the local coating thickness. If this assumption is not pertinent, then gravitational flow will result in thinning of the coating layer at the top and thickening at the bottom of a finite substrate. The distinction between the two processes may be useful for those desiring to calculate, for example, the degree of "wedging" on a dipcoated part as against simply calculating a sag length or sagging velocity. Again, in the case of sagging, h is assumed constant and a sagging distance x may be calculated, whereas, for drainage, the thickness h varies with distance x down the substrate. The equations describing the flow are otherwise identical and interchangeable. By a derivation similar to that of Wu [*68,72*] for sagging, the expressions below, describing drainage, can be obtained.

For a Newtonian liquid, the thickness at time t at a distance x down from the upper edge of the liquid layer is given by

$$h = \sqrt{\frac{\eta x}{\rho g t \cos\theta}} \tag{54}$$

The angle θ is as defined above. Most coatings are non-Newtonian, however, which will have great impact on the drainage behavior. For example, shear thinning fluids will drain to a much more uniform film thickness than Newtonian fluids. The gravity drainage of a power law fluid (see **Shear-Dependent Viscosity**) is given by

$$h = \left[\left(\frac{n+1}{n}\right)\left(\frac{x}{t}\right)\right]^{n/n+1}\left(\frac{K}{\rho g \cos\theta}\right)^{1/n+1} \tag{55}$$

In the above, K is the "consistency" term and n the exponent in the power law expression (see **Shear-Dependent Viscosity**). Here we see a practical application of mathematical flow models. The parameters obtained from fitting the power law to an experimental flow curve can be inserted into the above equation and the sagging behavior of a coating formula can be calculated and graphed. Figures 24*a* and 24*b* compare the drainage behavior of a Newtonian and a shear thinning liquid layer, showing film thickness as a function of both time and height on a vertical substrate (calculated with Eqs 54 and 55).[11] The improved uniformity of the non-Newtonian coating can clearly be seen. For shear-thinning fluids with yield stress, the drainage equation is

$$h = \left[\left(\frac{n+1}{n}\right)\left(\frac{x}{t}\right)\right]^{n/n+1}\left(\frac{K}{\rho g \cos\theta}\right)^{1/n+1} + \frac{\tau_0}{\rho g} \tag{56}$$

The constants n, K, and τ_0 are obtained by fitting the Herschel-Bulkley flow model to the experimental flow curve (see **Shear-Dependent Viscosity**).

As with leveling, a realistic description of sagging must include not only non-Newtonian effects, but also effects of drying, geometry of the applied film, and the instantaneous rheological state of the applied film. A recent review, analysis, and experimental study of sagging examines these effects [*67*].

[11]Note that $t = 0$ is excluded, since $h = \infty$.

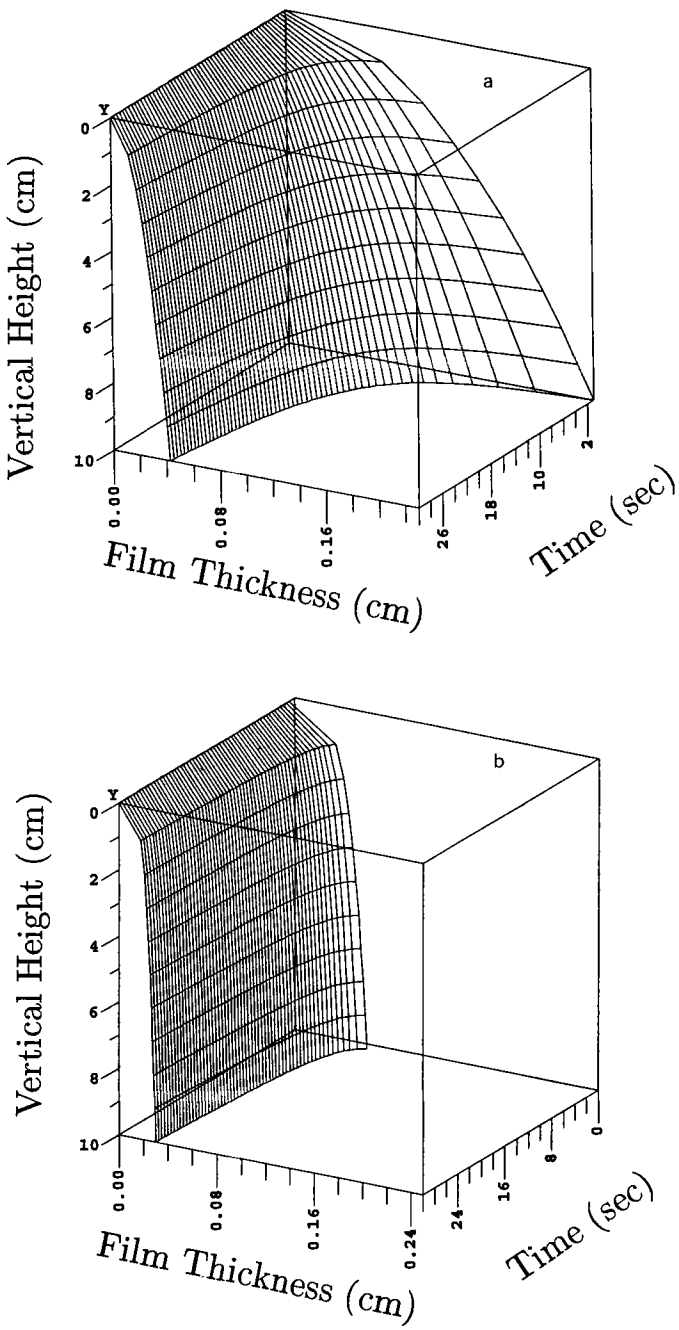

FIG. 24–(a) Drainage behavior for Newtonian fluid is represented three-dimensionally as film thickness versus vertical height versus time. Note that thickness varies strongly with height, known as "wedging"; (b) Drainage behavior for non-Newtonian (shear thinning) fluid is represented three-dimensionally as film thickness versus vertical height versus time. Note that thickness is nearly constant with height, showing that shear thinning rheology can achieve improved film uniformity in dip coating.

Measures of Sagging

A number of laboratory methods for evaluating sagging have been used, some of which measure some rheological property related to sagging behavior [*80*] and some of which measure sagging directly. Among the latter are ASTM D 4400, in which a drawdown blade with multiple slots (manufactured by Leneta) spreads paint stripes of graduated thicknesses over a nonabsorbent substrate. Sag is rated according to the thickest stripe that does not show sag (Fig. 25). A similar but somewhat simpler test involves the use of a wire device that scribes two lines, of ⅛ and ¼ in. (0.32 and 0.64 cm) width across a 3-wet-mil paint stripe, which is then hung vertically, and sagging is visually evaluated on the dry paint film.[12] The method is illustrated in Patton [*73*]. Another device which has apparently met with some success is the so-called "sagging balance" [*74*], which uses an electronic balance to measure the shift in mass accompanying drainage of a coating applied to an inclined plate.

Sagging is, of course, driven by gravitational shear stress. The sagging shear stress magnitude depends entirely on the wet film thickness and density (Eq 50). The resulting shear rate of sagging is determined by the rheology profile of the paint in question. It is imprecise to attempt to predict sagging from viscosity measurements at an arbitrary "sagging shear rate" and may lead to incorrect estimates of relative sagging. The proper way to predict relative sagging tendency is to plot viscosity as a function of shear stress rather than shear rate. Shear stress levels corresponding to the desired wet film thickness can be calculated, and the magnitude of the viscosity controlling sagging (η_{sag}) determined from the graph. Figure 26 compares two paints in this manner, with indicated gravitational shear stress levels corresponding to wet film thicknesses of 3, 6, and 12 mils film thickness indicated. Figure 27 shows flow curves for the same two paints plotted as a function of shear rate, with the calculated sagging shear rates at 3, 6, and 12 mils indicated ($\dot{\gamma}_{sag} = \tau_{sag}/\eta_{sag}$). The solid line in Fig. 27 indicates approximately the shear rate of the Stormer™ paddle viscometer. The ratio of the viscosities of the two paints at the Stormer™ shear rate is less than 2, whereas the ratio computed at the true sagging shear rates is as high as 6. Clearly, comparison of viscosities measured at an arbitrary shear rate can lead to incorrect predictions of relative sagging behavior, particularly if flow curves should cross over.

LEVELING

The mechanics of coating application generally cause the applied coating layer to be initially rough and consequently of varying thickness. Uniform film thickness is desired both for reasons of appearance (color and hiding uniformity) and for substrate protection (necessary minimum film thickness). The process of smoothing of the initial rough surface is called *leveling*. Adequate leveling is of obvious critical importance to the success of a protective or decorative coating; hence, a very large number of studies of the subject have been published (e.g., Refs *2,38,75–82*). Despite this, there is not complete agreement on how best to predict leveling behavior from rheological measurements. Leveling generally correlates reasonably well to low-shear viscosity, but not always because of complicating factors such as viscoelasticity, time dependence, volatilization, wicking, and surface tension gradients, which can greatly confuse the picture. The leveling and film formation of a paint layer is so complex that, in the opinion of

[12]Federal Test Method 4493, September 1965.

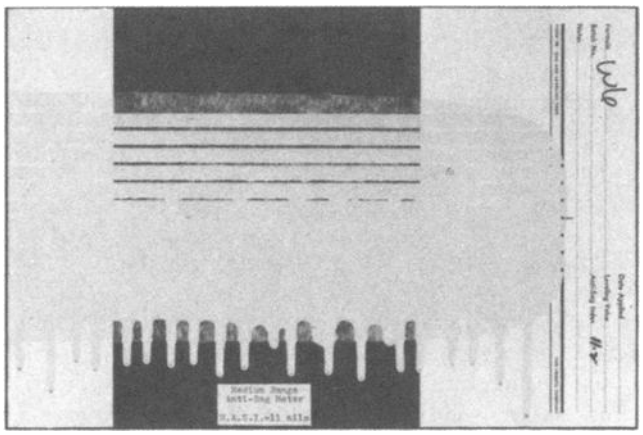

FIG. 25–Sagging evaluated by Leneta drawdown blade. Sagging is rated by the thickest paint stripe that does not show sag.

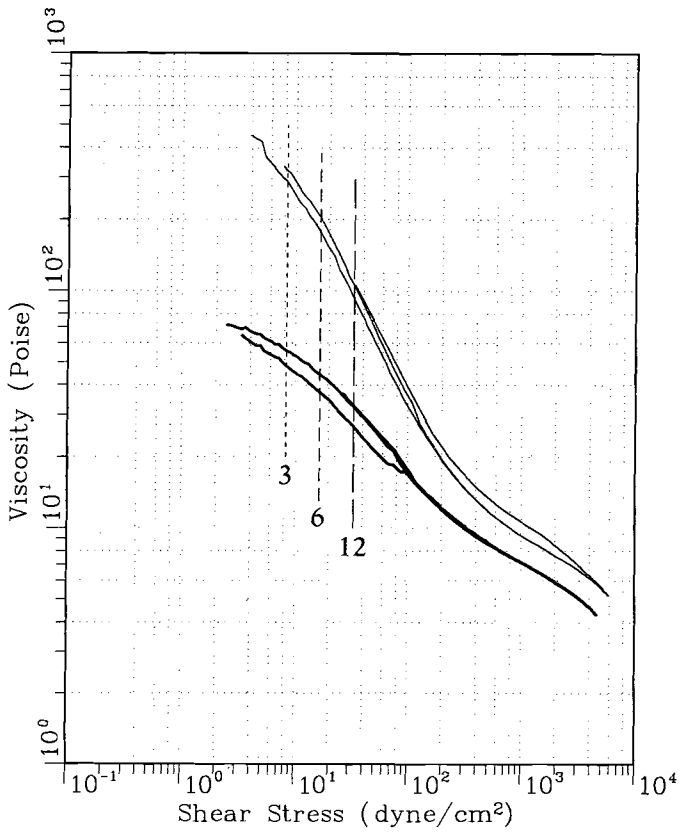

FIG. 26–Viscosity versus shear stress for two paints, together with lines indicating sagging shear stress acting on films of 3, 6, and 12 wet mils thickness. Relative sagging behavior is indicated by the ratio of viscosities at the appropriate film thickness. From this, $\dot{\gamma}_{sag} = \tau_{sag}/\eta_{sag}$.

this author, only computer modeling has the potential to provide a wholly satisfactory method of analysis and prediction (see, for example, Schwartz and Eley [*79*]). However, such modeling capability is not readily available to most practitioners, so we will review some of the analytical models of leveling. These can provide at least qualitative understanding of the role of rheology and other factors in leveling.

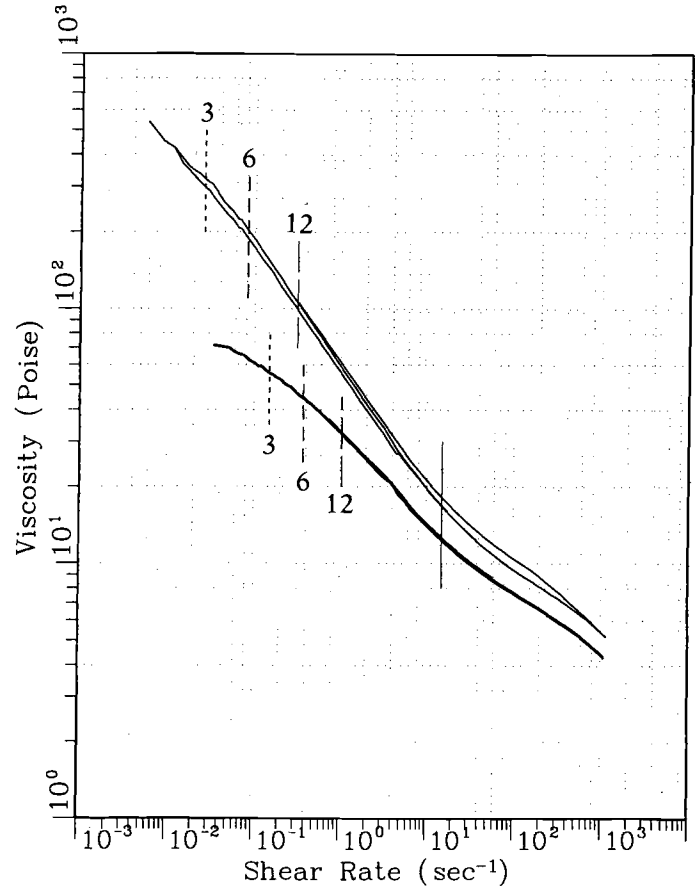

FIG. 27–Viscosity versus shear rate for two paints, together with lines indicating sagging shear stress acting on films of 3, 6, and 12 wet mils thickness. Solid line is approximate shear rate of the Stormer viscometer.

The mechanics of leveling is illustrated in Fig. 28 for a liquid without surface tension gradient, having a sinusoidal surface profile. The sum of all surface tension vectors in the curved surface produces a net force downward at the "peaks" and upward in the "valleys," the liquid-air interface acting as if it were a stretched elastic membrane. Forces due to liquid surface curvature are called *capillary forces* and result in capillary pressure variations within the liquid layer. Thus, leveling is driven primarily by capillary pressure gradients arising from local surface curvature under conditions of uniform surface tension. Liquid is "pumped" from the peaks into the valleys, ultimately producing a level surface. For thin films, gravity is of negligible effect on leveling unless a critical roughness wavelength is exceeded. For a typical paint, the critical wavelength is of the order of 1 cm [*84*].

The quantitative prediction of leveling from physical properties requires the use of some mathematical model of the process. Smith, Orchard, and Rhind-Tutt [*2*] derived such a model by a linear lubrication approximation-type analysis, assuming a uniform sinusoidal surface profile. (The Los Angeles Paint Club obtained a similar equation in 1953 [*83*] for surface roughness approximated by semicircular arcs.) Orchard later [*85*] developed a complicated expression for the leveling of a more realistic, arbitrarily rough surface profile in terms of a Fourier series. However, the expression simplifies considerably when the coating thickness is as-

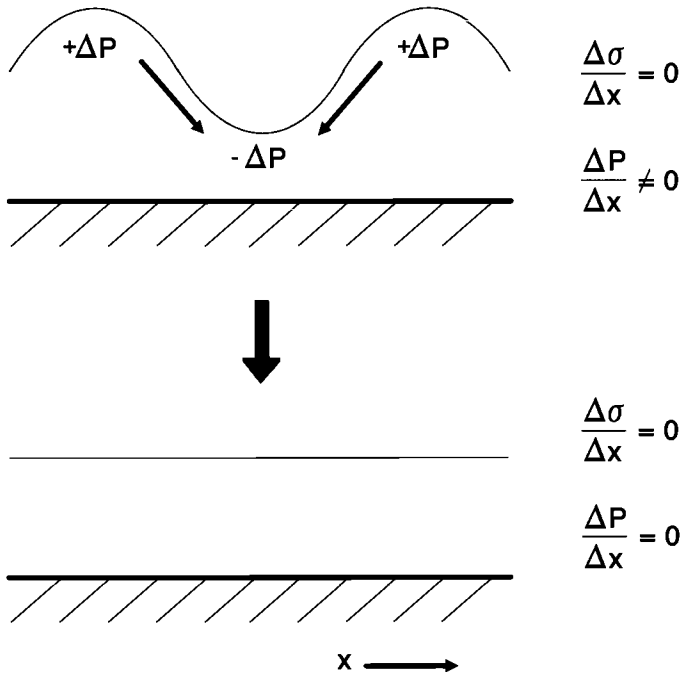

FIG. 28–Surface tension-driven leveling. Curvature of liquid surface generates capillary overpressures and underpressures, ΔP, which drive fluid flow to level the surface. There is no surface tension gradient along the film coordinate ($\partial\sigma/\partial x = 0$). Pressure is not uniform, however ($\partial P/\partial x \neq 0$).

sumed to be small relative to the roughness wavelength. Assuming a single sinusoidal wavelength (which is a reasonable approximation since the leveling behavior will be dominated by the longest wavelength), the Orchard equation is

$$\ln\frac{a_t}{a_0} = -\frac{16\pi^4 h^3 \sigma t}{3\lambda^4 \eta} \tag{57}$$

for constant surface tension σ and viscosity η. The equation indicates that the logarithmic ratio of surface wave amplitude a at time t to its initial amplitude a_0 depends on the coating layer thickness h to the third power and inversely on the wavelength of the surface roughness λ to the fourth power. For roughness geometry other than sinusoidal, the constant term $(16\pi^4/3)$ will take on other values.

The Orchard equation, as written above, is only an approximation to the leveling behavior of most real paints because it assumes Newtonian fluid behavior and neglects time-dependent (and other[13]) effects. The latter effects include thixotropy and changes in rheology from loss of solvent due to drying and also due to "wicking" (absorption) of the liquid phase into a porous substrate. Nevertheless, the Orchard model conveys the importance of film geometry and physical properties on leveling rates and allows an estimation of the order of magnitude of effects of changes in these variables. For example, it should generally hold, despite complicating factors, that doubling the wet film thickness will increase the leveling rate eight-fold. However, a more realistic description is warranted, taking into account other film properties and processes that affect leveling significantly. A step was taken by Murphy [*86*] (see also Refs *87* and *76*), who rederived the Orchard equation for pseudoplastic paints assuming power law behavior (see **Shear-Thinning Fluids**)

$$a^{(n-1/n)} = a_0^{(n-1/n)} - \frac{n-1}{2n+1}\left(\frac{\sigma}{K}\right)^{1/n} \left(\frac{2\pi}{\lambda}\right)^{(3+n)/n} h^{(2n+1)/n} t \tag{58}$$

This expression contains the power law coefficients, K and n, all other terms retaining the same definitions as above. Note that the leveling rate increases as the power law exponent, n, decreases (i.e., as the paint becomes more shear thinning). As expected, the leveling rate decreases with increasing K (consistency). Lu [*48*] found the Murphy equation valid for correlating the change of brushmark amplitude with time for systems where the leveling was clearly dominated by the viscosity. However, the Murphy equation still assumes that viscosity depends only on shear rate and that surface tension does not change during the leveling process. In reality, both will change due to evaporation of the volatile phase of the coating or to wicking. The Murphy equation may be modified to take account of time-dependent viscosity increase by including a time-integral expression for the viscosity

$$a^{(n-1/n)} = a_0^{(n-1/n)} - \frac{n-1}{2n+1}\sigma^{1/n}\left(\frac{2\pi}{\lambda}\right)^{(3+n)/n} h^{(2n+1)/n} \int_0^t \left(\frac{1}{\eta(t)}\right)^{1/n} dt \tag{59}$$

where $\eta(t)$ is some time function of viscosity relating effects of thixotropy, drying, wicking, etc. The effect of time-dependent viscosity on leveling is dramatic, as shown in Fig. 29. Here, for two different paints, the decay of surface amplitude is calculated using Eq 58 (Curves A) and Eq 59, together with an experimentally determined expression for the increase of viscosity with time due to drying (Curves B). Camina [*76*] reported that the viscosity of a drying paint increases exponentially in the initial stages. Therefore, an expression such as the following would fit drying-viscosity data

$$\eta(t) = \eta_0 e^{kt} \tag{60}$$

where η_0 is the viscosity before drying has begun, k a drying rate constant, and t the time. Such an expression can be inserted into Eq 59 in place of $\eta(t)$ and integrated[14] to calculate the leveling curve for a paint whose viscosity is increasing with time due to solvent loss. In fact, Eq 60 can account for all time-dependent effects if k is understood as the reciprocal of a sum of time constants representing all time-dependent processes [*78*]

$$k = \frac{1}{\tau_{\text{dry}} + \tau_{\text{wick}} + \tau_{\text{thix}}} \tag{61}$$

Here, τ_{dry} is the time constant (inverse of rate constant) for drying. Similar time constants can, in principle, be obtained

[13]Overdiep [*78*] has demonstrated that, for some solvent enamels whose leveling is influenced by surface tension gradients, the Orchard equation fails even to give a qualitative description of behavior.

[14]Provided that the viscosity during drying is measured at unit shear rate, K, in Eq 58 becomes η in Eq 59.

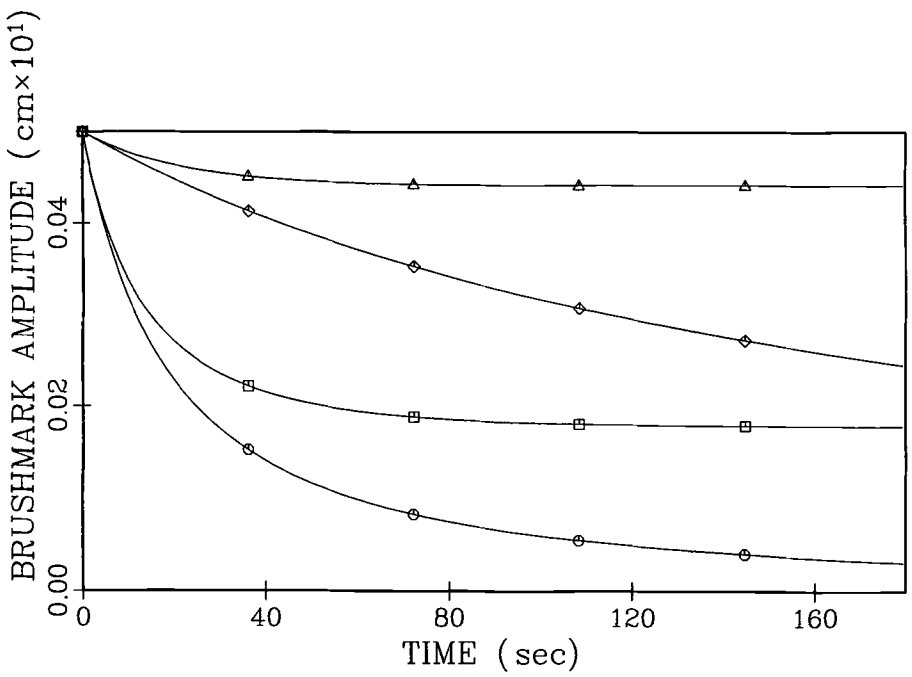

FIG. 29–Calculated brushmark leveling for two paints, with and without effects of drying. Curves calculated using Eqs 59 and 60: □—Paint A, with drying; ○—Paint A, without drying; △—Paint B, with drying; ◇—Paint B, without drying.

for solvent loss through wicking (τ_{wick}) and for viscosity increase due to thixotropy (τ_{thix}) (see *Thixotropy Test Methods*).

Quach [*84*] has discussed and summarized the shortcomings of various laboratory methods of leveling evaluation. As noted by Quach, much work on leveling has been done without adequately taking into account the numerous interacting subprocesses whose final result is the dried film profile. An additional important factor recently dealt with experimentally and theoretically is the influence of surface tension gradient-driven flows (Marangoni flows) [*78,88,90*]. Surface tension gradients may arise due to a number of causes during film formation and when present can have consequences for the course of film leveling, among other things. Figure 30 illustrates the mechanism of surface tension gradient-driven flow, which can result in the deleveling of an initially level liquid layer. Local surface tension gradients may develop due to differential evaporation or to temperature gradients (or other causes). This results in a surface flow from regions of low surface tension toward regions of high, in an attempt to reach surface equilibrium. The moving surface "drags" subsurface liquid along, creating a bulk flow. This is the Marangoni effect. The driving force for Marangoni flow in the case of differential evaporation is a shear stress tangent to the film surface, τ_s, proportional to the strength of the dependence of surface tension on solvent concentration, $\partial\sigma/\partial[S]$, and to the magnitude of the solvent concentration gradient, $\partial[S]/\partial x$ (x is the film coordinate). Hence

$$\tau_s = \frac{\partial\sigma}{\partial[S]}\frac{\partial[S]}{\partial x} = \frac{\partial\sigma}{\partial x} \tag{62}$$

the surface tension gradient $\partial\sigma/\partial x$ drives the flow. For the case of Marangoni flow driven by thermal surface tension gradients, replace $\partial[S]$ by ∂T in the above. Persistence of surface tension gradients until the film is incapable of reflow

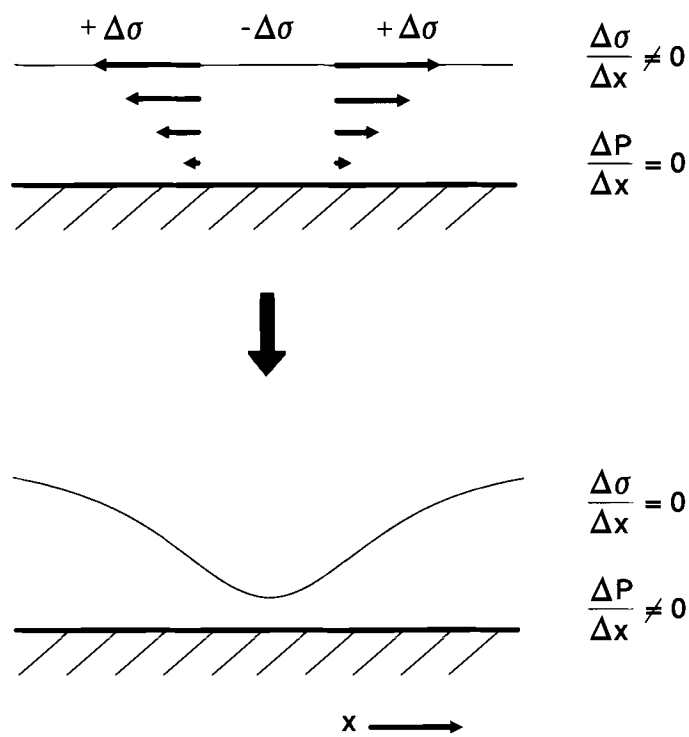

FIG. 30–Deleveling by Marangoni (surface tension gradient-driven) flow. Surface tension gradient ($\partial\sigma/\partial x \neq 0$) drives surface flow, resulting in bulk flow and deleveling of initially level surface.

will result in an appearance defect. Overdiep [*78*] demonstrated (for solvent-based paints) that Marangoni flows initially enhance the leveling rate, but can produce a "rebound" effect that ultimately worsens film roughness. Wilson [*90*]

recently modeled this behavior by a linear perturbation analysis. Other authors have discussed the importance of Marangoni flows for waterborne, cosolvent-containing coatings [*79,89*].

The role of viscoelasticity in leveling has been a subject of some debate, with some authors concluding that elasticity enhances leveling [*91*] and some that it retards leveling [*38,92*]. The evident link between elasticity and the underlying structural rheology for coatings (see **Viscoelasticity and Industrial Processes**) suggests the presence of a gel-like structure of some sort in systems possessing significant elasticity. Such a structure would be expected to inhibit flow at low stress levels so that coatings which exhibit elasticity should also show poorer leveling. In any case, the leveling behavior of viscoelastic systems has been modeled by Keunings [*38*] and the presence of viscoelastic relaxation shown to retard leveling. The leveling rate, α, as a function of the Newtonian leveling rate, α_{Newt}, was shown to be

$$\alpha = \frac{\alpha_{\text{Newt}}}{1 + \lambda\alpha_{\text{Newt}}} \tag{63}$$

where $\alpha = da/dt$ (rate of change of roughness amplitude, a, in s^{-1}), and λ is the elastic stress memory time constant (or relaxation time) (see *Viscoelastic Models*). In Eq 63, the Newtonian leveling rate is always positive, hence elasticity ($\lambda > 0$) always retards leveling. Interestingly, if surface tension gradients are present, α_{Newt} may actually become negative (i.e., deleveling, or crawling). In such cases, late-developing elasticity will be of benefit by retarding the deleveling. Table 4 shows the results of a calculation similar to that of Keunings adapted for the case of a typical paint. It is seen that the leveling rate dramatically decreases and the leveling half-time increases (by a factor of 3500), relative to the Newtonian ($\lambda = 0$) values, for $\lambda = 100$ s.

Measures of Leveling

Visual evaluation of leveling is common practice. However, it is generally agreed that visual rating is subjective to the degree that leveling rankings are often found to be operator-dependent. Numerous objective methods and standards have been published. Quach [*84*] reviewed aspects of both scientific and laboratory practical studies of leveling. For the latter, special drawdown blades have been used such as the NYPC leveling test blade (ASTM D 2801), which has pairs of notches over a range of depths. Leveling is judged by the flowing together of adjacent paint stripes. This method has been criticized by Quach and others [*27*] because the paint passing through the notches experiences a varying shear rate due to varying notch depth, resulting in a different shear history for each stripe, and because the shear rate achieved is unrealistically low. The latter test has been superseded by ASTM D 4062, based on a grooved drawdown rod. In this method, the paint is presheared, simulating brushing shear rates, by ejection from a syringe and 15-gauge needle prior to drawdown. The leveling quality is then estimated by visual comparison of the dried film with plastic leveling standards viewed against oblique lighting.

Kornum [*93*] gives a good discussion of issues of measurement under test conditions approximating real paint processes, including leveling. Dodge [*27*] also emphasizes that the best rheological test for leveling should most closely simulate the application experience of the paint. This means: (1) the paint should experience shear rates/stresses of similar magnitude and duration to those of the application process; (2) the shear rate/stress should then be step-changed to values representative of the leveling process; (3) the change of viscosity with time should then be followed under the latter conditions. This protocol is essentially identical to the "step-shear" method of characterizing thixotropic recovery described in **Thixotropy Test Methods.** This kind of procedure is most easily accomplished by employing a rheometer capable of "job streaming" or "linked methods." However, the foregoing method still suffers from the limitation that the effect of drying on viscosity during the leveling period is neglected. Figure 29 demonstrates that this can be a very significant effect. Paints "A" and "B" were commercial formulas which differed markedly in leveling performance. The increase of viscosity with time during drying of a film of typical applied thickness was measured for both and found to obey Eq 60. The latter expression was then inserted into Eq 59 as the time-integral function for viscosity (as described in the previous section) and the leveling curves in Fig. 29 were calculated. There are two curves for each paint, one showing how the paint levels without the effect of drying, and one calculated taking the increase of viscosity due to drying into account. The effect of drying is most dramatic on Paint B, where the reduction of surface roughness achieved after 3 min decreases from 50 to 10%.

It is established that leveling shear stress decays exponentially as leveling progresses [*80*]. A controlled-stress rheometer with programmable logarithmic stress ramps offers the ability to simulate the variation of viscosity with realistic shear-stress decay using variable ramp times. Leveling efficiency might then be judged by numerically integrating the fluidity over the "leveling" period.

$$\Phi = \int_0^t \frac{1}{\eta} dt \tag{64}$$

The leveling might be expected to be logarithmically related to the fluidity integral [*81*].

A very promising method for direct observation of paint leveling has been described by Klarskov [*82*]. It is an optical interferometric method which is simple but quite precise for real-time surface profile measurement, having a vertical resolution of a fraction of a micron. At present, unfortunately, there is no commercial instrument based on Klarskov's method.

ATI Systems[15] offers a relatively inexpensive noncontacting Laser profilometer. Laser confocal microscopes can also measure the real-time evolution of surface profile during leveling, but are quite expensive.

RHEOLOGY INSTRUMENTATION

There are a great many instruments that have been devised to measure viscosity or "consistency." However, a number of them have in common a serious limitation in their design

[15]ATI Systems, Inc., P.O. Box 71460, 32355 Howard Street, Madison Heights, MI 48071.

which makes them generally unsuitable for measurements of non-Newtonian fluids. The importance of this issue becomes apparent when it is realized that the majority of coatings and coatings components are non-Newtonian, yet many laboratories continue to use methods which are not suited for such materials. The difficulty with many of the "traditional" laboratory viscometers is that the "flow field" (the total description of the trajectories of the fluid elements) is complex and not subject to practicable mathematical description. The result is that an accurate strain rate cannot be calculated. Therefore, even if the stress is known, the true viscosity cannot be obtained. Furthermore, the shear field is often so nonuniform that, for non-Newtonian materials, the viscosity of the material itself varies within the test sample. For complex flow fields, such an error cannot be corrected. The measurement error will be in proportion to the deviation from Newtonian character. Nevertheless, such instruments have been in use throughout the industry for decades and no doubt will continue to be used for the foreseeable future. The approximate measurement given is somehow related by the practitioner to something believed relevant to the performance. One suspects that when the result is contradictory, as is probably often the case, it is either ignored or "worked around." We shall refer to this type of device as a "Q/C (quality control) instrument" or a "qualitative viscometer." It should be emphasized that these instruments are accurate for Newtonian or near-Newtonian materials and are generally useful as Q/C test devices even when the measurement is approximate. However, the practitioner should be alert to situations where their deficiencies can be of significance.

In years past, many coating fluids were nearly Newtonian, which accounts in part for the success of Q/C-type instruments. As alluded to before, it is very easy to characterize a Newtonian fluid. Virtually any type of flow measurement device may be used to obtain accurate information on the viscosity of such a material provided the device used is calibrated with known standard fluids and the temperature is controlled. It is not even necessary to know the shear rate of the measurement since Newtonian fluid viscosity is independent of the shear rate. Consequently, Newtonian viscosity measured by any test is valid for all process conditions (except turbulent flow). Even instruments which measure viscosity according to some arbitrary scale may be used since they may be calibrated in absolute units using Newtonian standard fluids.

A requirement for an instrument to measure non-Newtonian fluids properly is that the flow field within the test fluid be viscometric, defined as "everywhere indistinguishable from steady simple shear" (or other ideal deformation) [*1*]. Instruments which measure under such well-controlled conditions we will call "research instruments." Nonviscometric flows such as tube flow can be used for non-Newtonian fluids when necessary corrections are applied.

Q/C INSTRUMENTS

These are of three types: (1) efflux devices, (2) rotational devices, and (3) obstructed-flow devices (following Barnes et al. [*94*]).

Efflux Devices (Orifice flow)

Efflux devices, or orifice cups, come in a variety of types, but share one principle: measuring viscosity by flow from a reservoir or cup through a restriction of some type. In most cases, the restriction is simply a hole in the bottom of the reservoir, but in some it is a short tube. These devices have the advantages of low cost, ease of cleaning, durability, and simplicity in the measurement, which is simply the time to empty (in whatever manner "empty" is defined). They also have, however, a number of limitations. The first is that the flow is never viscometric. Even when a short capillary tube is the exit, the length-to-diameter ratio is too small for proper tube flow to develop, so that the flow is dominated by entrance effects. In fact, the orifice cups have been described as "poor capillary viscometers." Since substantial shear stress is not developed in the exit hole, orifice cups are not suitable for very thin liquids because a significant fraction of energy is dissipated not in viscous flow, but merely in accelerating the fluid. In other words, measurements on low viscosity fluids are subject to significant fluid inertia errors. Thus, for the Ford No. 4 Cup (ASTM Method D 1200), liquids with an efflux time of less than 20 s should not be used. The flow in efflux cups is stress-driven, controlled by the hydrostatic head, i.e., the fluid depth in the cup. The pressure varies as the liquid drains; consequently, the flow rate (shear rate) varies during the test. The viscosity of shear-thinning liquids, therefore, will increase in the course of the test, and in extreme cases such materials may not fully drain from the cup. Because the flow field is complex, the shear rate cannot be calculated, and from the previous argument will depend on the viscosity-shear stress relationship for non-Newtonian materials. For the above reasons, it must be concluded that orifice cups are really only suitable for viscosity measurements of Newtonian liquids of moderate viscosity. Non-Newtonian liquids should not be tested unless only mildly shear-dependent. Materials with possible yield stress (meaning any thixotropic materials) should not be tested with efflux devices. A final caution for these devices is that, unless the temperature of the cup is controlled by means of a water jacket, large errors are likely to result. Even if the test liquid is thermostatted in a water bath prior to test, it can rapidly change in temperature and viscosity when placed in a cup which is at the temperature of the room. Figure 31 shows data for replicate measurements on cups with and without temperature control. Obviously, the errors in the data taken with the standard cup would hide the real batch-to-batch differences of the product. A good Q/C test should reveal, not obscure, product variability.

Rotational Devices

Stormer™ Viscometer

The widely-used Stormer[16] Viscometer was one of the earliest controlled-stress rotational viscometers. Rotors of various geometries are available, but the "paddle" rotors, in which two paddles are attached in offset fashion to a rotating shaft, are exclusively used for the measurement of the consistency of paints. During a measurement, the rotation is driven by a

[16]The name "Stormer" is a trademark of the Thomas Scientific Company.

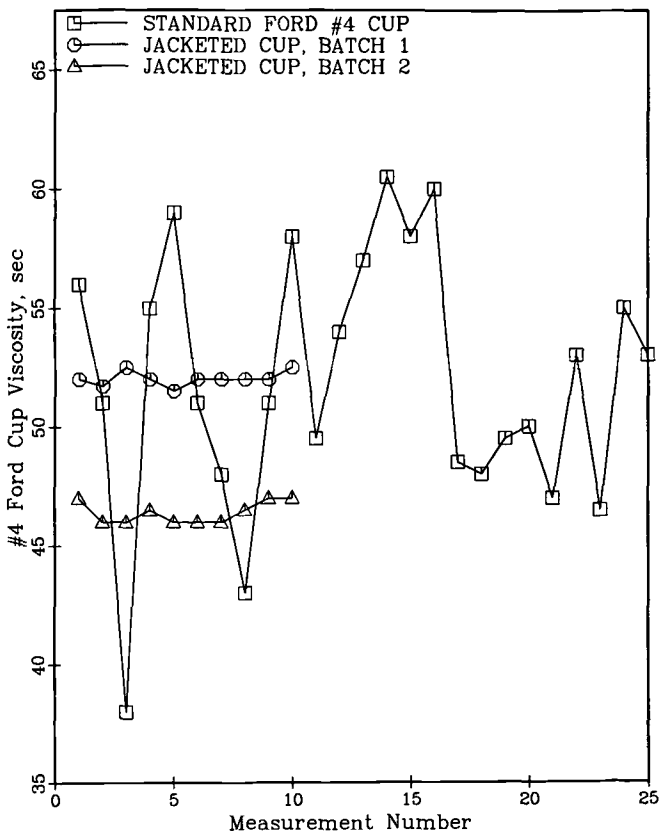

FIG. 31—Ford cup viscosity data taken with and without temperature control of the cup. Test temperature was 130°F (54°C).

free-falling weight attached to a string and pulley arrangement, the string being wound around a drum. The shear stress is varied by use of different weights. A counter tallies up the number of revolutions as the weight falls. After the first ten revolutions, the time required for the next 100 is measured. (Stroboscopic timers are available.) The apparent viscosity is calculated from a plot of applied torque versus rotor rpm. The measurement is also made in terms of the weight, W, required to achieve a rotational speed of 200 rpm. The viscosity is obtained according to an arbitrary scale called "Krebs Units" (KU). A conversion table of W versus KU is supplied. As with any viscometer whose measurement geometry is complex, an absolute viscosity (i.e., in engineering units of poise or pascal-seconds) cannot be calculated with this instrument for non-Newtonian fluids. The Stormer viscometer is specified in a number of standard test methods.[17]

For its purpose, i.e., to measure the in-can "feel" of paint, the Stormer is a very good viscometer, that is, the Stormer measures while stirring the paint with a constant force, just as the consumer would. Thus, the instrument satisfies the criterion of measuring under conditions closely approximating those of the process. This justifies the use of an arbitrary measurement scale, in this case, and makes the Stormer a valuable component of the paint laboratory. The only caveat would be not to violate the above-mentioned principle by attempting to use Stormer data to predict paint performance for a process which is far removed from the flow kinematics of the instrument.

Thomas-Stormer™ Viscometer Model ETS-1000

This instrument is an electronic implementation of the Stormer paddle viscometer by the Thomas Scientific Company.[18] Weights are done away with, as the instrument is motor-driven. A selector switch allows a digital readout to display the measured viscosity in centipoise, Krebs Units, or in grams (for comparison to the standard Stormer instrument).

Brookfield Digital Viscometer Model KU-1

The Brookfield Model KU-1 is likewise an electronic paddle viscometer, similar to the Stormer, by Brookfield Engineering Laboratories. A digital panel readout displays either the weight in grams corresponding to the applied motor torque or the viscosity in Krebs units (KU).

ICI Rotothinner

The Rotothinner, originally developed by ICI Paints, is driven by a constant-speed motor and utilizes a large, disk-shaped rotor which is immersed in the sample under test. A standard sample container is used, which is held magnetically to a turntable. The torque transmitted through the sample rotates the turntable until a steady position is reached. (The rotary motion is resisted by a spring.) The turntable is graduated in poise units, and the viscosity is indicated by a pointer attached to the instrument base. The viscosity range of a given model is somewhat narrow, and measurement over a wide viscosity range necessitates purchase of separate instruments. The instrument is calibrated for use only with standard containers. There is no provision for temperature control of the specimen. For "rheologically structured" materials, the manufacturer recommends to allow up to 4 min under shear for the reading to become steady, thus providing for a more or less constant shear history. However, temperature may vary during this period due to the input of energy resulting from the 575-rpm rotor speed.

Although the instrument has a scale graduated in poise units, the shear rate of test is unknown since the flow field is not viscometric. Flow in the vicinity of a rotating disk can be quite complex, especially for non-Newtonian and viscoelastic materials. Consequently, the apparent Rotothinner viscosity must be considered only approximate and the scale graduations arbitrary for such materials.

The Rotothinner is manufactured by Sheen Instruments, Ltd. and is widely used in Europe.

Obstructed-Flow Devices

These are gravity-driven instruments in which flow is due to density differences between the test fluid and a falling object (falling ball viscometer, falling needle viscometer) or a rising bubble (bubble tube viscometer). In each case, the fluid has to flow around the moving object; hence, they are classed as obstructed-flow devices. In the falling ball and rising bubble instruments, the flow field is complex with the conse-

[17]Test methods include ASTM D 115, D 562, D 816, D 856, D 1084, D 1131, D 1337, D 1338, and Federal Test Methods 3011.1, 3012, 3018, 3019, 3022, and 4281.

[18]The Thomas-Stormer ETS-1000 is available from the Cannon Instrument Company.

quence that these devices are generally not useful for non-Newtonian fluids. The falling needle viscometer, however, possesses a well-defined flow field [*95*], is therefore suitable for non-Newtonian materials, and will be discussed in the section on Research Rheometers.

Falling Ball Viscometer

A ball falling in a viscous fluid will reach a terminal, or constant, velocity U_∞, which depends on the density difference of the sphere and the liquid, the diameter of the ball, d, and the fluid viscosity, η. The viscosity of an unknown fluid may be calculated from the Stokes equation

$$\eta = \frac{(\rho_s - \rho_l)gd^2}{18U_\infty} \tag{65}$$

where g is gravitational acceleration. This deceptively simple method has several drawbacks, however. For one, the Stokes solution is only valid for low Reynolds numbers (viscous forces controlling, rather than fluid inertia, i.e., slow flow), and for low-viscosity fluids the ball density must be small enough to produce correspondingly slow rates of fall. For another, a wall correction may be needed to account for the interference of the container wall with the flow field of the ball and hence its falling rate. Perhaps the greatest difficulty, however, is the fact that the flow field around a moving sphere is complex, and when the fluid is non-Newtonian the complexity becomes mathematically intractable. Therefore, for non-Newtonian fluids, the falling-ball apparatus will not yield absolute viscosity, and the results would not be expected to correspond with those from an instrument having viscometric flow geometry. A solution to the above problems is provided by a relatively new instrument called the falling needle viscometer (see below).

Rising-Bubble Viscometers

If certain flow field assumptions are made for a rising air bubble in a liquid, the viscosity of the liquid can be calculated from [*42*]

$$\eta = \frac{1}{3}\frac{\rho g R^2}{v} \tag{66}$$

where ρ is the liquid density, R the radius of the air bubble, and v the rising velocity. However, the calculation is only approximate because the air bubble shape often deviates from the assumed sphericity due to buoyancy. Furthermore, if the liquid phase were non-Newtonian, significant errors would result for which there is no correction available.

The Gardner-Holdt bubble tubes provide a rapid means of estimating the kinematic viscosity (see **Capillary Viscometers**) of transparent liquids such as varnishes and resins using the rising bubble principle. These consist of a series of sealed glass tubes containing mineral oils comprising a range of standard viscosities. The test liquid is placed into a similar tube (ensuring the contained air bubble is the same volume) and thermostatted in a water bath. The test material and a rack containing the standard tubes are inverted, and the test viscosity is identified according to the letter (or sometimes number) designation of the standard tube whose rate of bubble rise is nearest the same. Interpolation between the standards is sometimes done. Bubble tubes are disposable, easy to use, and the results can be converted to kinematic viscosity by means of tables. Bubble tubes can be used also to measure resin color. For process resins nearing the gelation point, the bubble can display a pointed "tail," or pronounced "teardrop" shape, an indication of the onset of viscoelasticity. As a reference for the use of the Gardner-Holdt method, see ASTM D 803.[19]

RESEARCH RHEOMETERS/VISCOMETERS

Research-quality rheometers are of several types, chiefly employing: (1) steady rotational shear, (2) dynamic (oscillatory) shear, and (3) capillary tube flow. Acoustic wave devices constitute a fourth, less common, type. Useful summaries of instrumentation and methods are found in Refs *96–98*. Although dated, Van Wazer's book is still a valuable source [*42*]. Appendix A lists vendors of research rheometers and viscometers.

Rotational Instruments

Controlled Stress and Controlled Rate

There are two basic types of rotational viscometers, which work in the following ways: (1) apply a controlled rotation rate and measure the opposing viscous torque, or (2) apply a controlled torque and measure the resulting rate of rotation. In the first case, which may be termed "controlled-rate," the applied angular velocity is the independent variable and the viscous drag torque the dependent variable. In the second case, termed "controlled-stress," the applied torque is the independent variable and the measured angular velocity the dependent variable. Instruments of the controlled-rate type include, for example, the Brookfield Synchro-Lectric Viscometer, Haake CV, Rheometrics RFS, and Bohlin VOR instruments. Instruments of the controlled-stress type include the Carri-Med CSL, Rheometrics DSR, Bohlin CS, Haake RS, and Physica MC rheometers.

The choice between the two types of instruments depends on the material under test and the kind of results desired. For characterizing highly structured materials or "weak gels" (e.g., thixotropic alkyds and unstable colloidal systems such as some pigment dispersions, thixotropes, etc.), the controlled-stress instruments are likely to be more appropriate. The reason is that controlled-rate instruments impose a shear field upon the specimen over a relatively short time scale, say, in the course of a shear rate ramp experiment. The resulting relatively rapid deformation tends to destroy shear-sensitive structure very quickly, making it difficult to gather much information about the structure. In contrast, with controlled-stress instruments, the applied stress can be gradually increased, allowing the specimen to "obey its own rules" of stress-strain (rheological) behavior, thus resolving the maximum amount of information. This is particularly true when one is concerned with materials possessing an apparent yield stress. Controlled-stress instruments can, in principle, directly measure the stress at the onset of yield, avoiding errors associated with indirect methods of yield stress measurement (see *Yield Stress Test Methods*).

[19]Additional standard test methods using bubble tubes are: ASTM D 1131, D 1545, D 1725, and Federal Test Method 4271 (141-a).

In selecting the appropriate instrument type, one should take into account also the type of coatings process in question. Some coatings processes are stress-controlled (or stress-limited), and some are rate-controlled (or rate-limited). A stress-controlled process is one whose shear rate is determined by the rheology of the material; that is, a relatively small amount of force drives the process, and the rate of the process is therefore determined by the viscosity of the material at the process shear stress. For example, different paints at a given wet-film thickness experience a constant gravitational shear stress, but will sag at different velocities depending on their viscosities at the sagging shear stress. A rate-controlled process is one whose shear rate is independent of the material rheology, that is, the available driving force is so large that the process rate or throughput is essentially not affected by viscosity. Examples of stress-controlled coatings processes and their driving forces include sagging (gravity), leveling (surface tension), particle settling (gravity), and airless spraying (hydrostatic pressure). An example of a rate-controlled process would be industrial rollcoating.

Since many coatings processes are stress-controlled or stress-limited, the controlled-stress rheometer offers the advantage of more convenient simulation of these processes. For example, a constant stress (simulating sagging) or a programmed exponential stress decay (simulating leveling) may be conveniently applied with the latter-type instrument. One capability unique to controlled-stress rheometers is the creep test, whereby a constant load is applied to the material and the deformation is recorded with time.[20] Creep has been found to be very useful, both for characterizing viscoelastic materials (see **Viscoelastic Models**) and for determining Region I of the equilibrium flow curve (see **Shear-Thinning Fluids**). The latter is obtained by applying a series of very low torques and measuring the equilibrium strain rate. The equilibrium flow method permits viscosity measurements to be made at the lowest possible rate of shear. A limiting factor in the accuracy of such methods, however, is the ability to minimize or correct for spurious air bearing torque.

Other advantages of controlled stress over controlled rate have been pointed out by Gleißle [*99*]. For example, using data for polymer melts, he demonstrated that measurements at constant stress are of greater sensitivity and better able to discriminate among materials than measurements at constant shear rate. Furthermore for controlled stress, the sensitivity, in terms of both absolute and relative measured viscosity differences among materials, is independent of the stress level chosen, unlike for controlled rate. In fact, the ratios of viscosities of two different materials, A and B, are independent of the shear stress

$$\frac{\eta_A(\tau_1)}{\eta_B(\tau_1)} = \frac{\eta_A(\tau_2)}{\eta_B(\tau_2)} \tag{67}$$

where τ_1 and τ_2 are two arbitrary stress levels. Since this would also hold true at low stress levels where the viscosity is constant, we are led to a very useful relationship: that the ratio of the shear rates for A and B, measured at a given shear stress, gives the inverse ratio of the zero-shear viscosities of the two materials.

$$\frac{\dot{\gamma}_A(\tau)}{\dot{\gamma}_B(\tau)} = \frac{\eta_{0,B}}{\eta_{0,A}} \tag{68}$$

The value of this fact to experimentalists is considerable. For example, it is often difficult to accurately measure η_0 for very low- or very high-viscosity fluids because of limited instrument range, sensitivity, or accuracy. Let us suppose $\eta_{0,A}$ is measurable but $\eta_{0,B}$ is not. However, reliable data for Material B are obtainable at higher (or lower) shear stresses, where the instrument is accurate. Equation 68 allows us then to calculate the unknown zero-shear viscosity, $\eta_{0,B}$. As another example, many dispersions, particularly those of importance to coatings, are colloidally unstable with the result that the zero-shear viscosity may not be measurable (see **Shear-Thinning Fluids** and Fig. 5). A similar technique to the above may obviously be used to obtain an inferred value of η_0 for such a system as it would be in the absence of the instability by comparison to another, colloidally stable material.

Gleißle also showed that the local flow exponent, n (see **Shear-Dependent Viscosity**), is constant at constant shear stress, independent of differing material rheology. As a consequence of this, the Weissenberg-Rabinowitsch correction to the capillary viscosity for non-Newtonian fluids becomes a constant at a given shear stress, independent of material rheology, since it depends only on the value of n (see **Capillary Viscometers** and Eq 11).[21] Gleißle's findings are apparently empirical and will need to be verified for systems other than the ones reported.

Inertia Correction

It can be particularly important for rotational rheometers of the controlled-stress type to correct the data for inertia error. If the test fluid is low in viscosity, and/or the test rotor has a large moment of inertia, and/or the acceleration is too high (short ramp time), a significant portion of the applied torque is dissipated not viscously, but in the acceleration of the rotor. A correction for this error has been published by Krieger [*100*]. Some commercial controlled-stress instruments now feature on-line inertia correction.

Brookfield Viscometers

Brookfield Synchro-Lectric

The Brookfield Synchro-Lectric viscometer utilizes a set of spindles or disks as the rotor/sensor, which are rotated in the test fluid at selected rpm's, so that the apparent viscosity may be measured at several shear rates to obtain a flow curve. Its advantages include low cost, simplicity of use, ease of cleaning, and durability. The instrument is in wide use throughout the industry and is the basis for a number of ASTM test methods.[22] It is included here in the list of "research quality" viscometers because the viscosity can be reported in absolute units over a range of shear rate, although often it is not (see below). Its limitations include the latter fact, plus that tem-

[20]Correspondingly, only controlled-rate instruments can perform a step-strain or stress relaxation test.

[21]This would also hold true of the Burgers correction to the parallel-plate viscosity of non-Newtonian fluids for the same reason.

[22]These include ASTM D 115, D 816, D 1076, D 1084, D 1286, D 1337, D 1338, D 1417, D 1439, D 1638, D 1824, D 2196, D 2364, D 2393, D 2556, D 2669, and Federal Test Method 4287.

perature control is not integral to the instrument. The Synchro-Lectric is available with digital output, automatic viscosity calculation, and computer-interfaced versions with analysis and graphing software.

Brookfield spindle viscometer measurements suffer from the use of arbitrary or nonfundamental units in reporting the result. Even though the viscosity is reported in absolute units (cP or mPa·s), the shear rate is not. Thus, both the spindle speed (rpm) and the spindle identity must be reported along with the measured viscosity. The measured viscosity can be different at the same rpm if a different size spindle is used. Without knowing the actual shear rate of measurement, a true flow curve cannot be constructed from the results. The true flow curve is desirable for several reasons, among them the possibility of comparison with results from other instruments, the quantitative description of the sample rheology by use of mathematical flow models and the subsequent application of such models to predict paint performance (see **LEVELING** and **SAGGING** for example). Methods for calculation of the corrected shear rate for Brookfield RVT spindles were given by Williams [*101*] and also Pierce [*102*]. Smith [*87*] has given a simplified method. (See also Ref *22*, pp. 28–31.) Some of the foregoing issues are at least partially answered with certain accessories available from Brookfield. These include options which have small-gap bob-in-cup geometry and temperature control, e.g., the small-sample adapter.

Wells-Brookfield Cone and Plate Viscometer

Brookfield also offers an instrument possessing a well-defined geometry and good temperature control—the Wells-Brookfield cone and plate viscometer. Its operation and appearance are very similar to the Synchro-Lectric, except the lower end has been modified to mount a cone and plate geometry with integral temperature control via a water jacket. Because the true shear rate can be calculated from the cone geometry and rpm, the viscosity of non-Newtonian materials can be measured in absolute units and an equilibrium flow curve determined. This instrument, therefore, is recommended over the standard Synchro-Lectric for routine viscosity measurement.

ICI Cone and Plate Viscometer

The ICI cone and plate viscometer is a relatively high shear rate instrument capable of absolute viscosity measurement. It is normally sold in a room-temperature, single-speed configuration. Temperature control is integral to the instrument, but there is no provision for control of solvent loss from the sample. This can be improvised, if desired. A high-temperature version is available, which is useful for resin melt viscosity measurement. The chief use of the instrument has been the measurement of viscosity at a shear rate of approximately 10 000 s^{-1} for the prediction of brushability. (See ASTM method D 4287 for high-shear viscosity by ICI cone and plate.)

Brookfield CAP 2000 Viscometer

The Brookfield CAP 2000 multispeed digital cone-plate viscometer was very recently introduced. It is very similar to the ICI cone and plate viscometer, but represents an improvement in that it is capable of variable shear rate measurement (to 24 000 s^{-1}). It also provides a digital display of viscosity and temperature as well as a data interface to a personal computer or data logger with applications software.

Falling-Needle Viscometer

This is an "obstructed-flow" device which utilizes a long, slender needle as the falling object. In so doing, it overcomes the objections to the falling ball viscometer while retaining the latter's simplicity of operation and relatively low cost [*103*]. The needle is hollow (allowing a wide range of needle densities) with hemispherically capped ends. End effects due to the finite needle length are mathematically correctable. This geometry produces a well-behaved flow field known as "annular-ducted flow," with the central tube (needle) moving at constant velocity. Because of the well-defined flow field, the true velocity gradient between the needle and container wall can be obtained, and the instrument therefore is suitable for measurements of non-Newtonian fluids [*104*]. The falling-needle viscometer may be especially useful for determination of very low shear stress or shear rate behavior of non-Newtonian fluids, for example the zero-shear viscosity (Region I of Fig. 3) and measurement of yield stresses [*105*].[23]

Capillary Viscometers

Capillary tube flow is a classical viscometric method which is useful for coatings in two main ways. Capillary viscometry is the method of choice for measurement of intrinsic viscosity (ASTM Method D 445) (see also **DISPERSION RHEOLOGY**) and also the measurement of very high shear rate rheological properties (see below).

For fluid flowing through a tube, the shear stress at the tube wall is

$$\tau_w = \frac{\Delta PR}{2L} \tag{69}$$

where ΔP is the decrease in pressure occurring over tube length L of radius R. The shear rate at the tube wall for a Newtonian fluid is given by

$$\dot{\gamma}_w = \frac{4Q}{\pi R^3} \tag{70}$$

where Q is the volumetric flow rate (cm^3/s). The viscosity is then

$$\eta = \frac{\tau_w}{\dot{\gamma}_w} = \frac{\pi R^4 \Delta P}{8LQ} \tag{71}$$

which is the well-known Hagen-Poiseuille equation. For applied pressure-driven capillary flow, particularly for high-shear measurements, a correction to Eq 71 is required because the fluid undergoes a large acceleration as it enters the capillary. Therefore, part of the energy loss represented by the pressure drop ΔP is in accelerating the fluid. This would result in a calculated viscosity which is too high and so necessitates a subtractive term or kinetic energy correction

[23]A new ASTM method for falling-needle viscometry is D 5478.

$$\eta = \frac{\pi R^4 \Delta P}{8LQ} - \frac{m\rho Q}{8\pi L} \tag{72}$$

where ρ = fluid density and m is a constant which is equal to unity for Newtonian fluids. For non-Newtonian fluids obeying the power law (see **Shear-Thinning Fluids**), m is calculated from

$$m = \frac{3(3n + 1)^2}{(4n + 2)(5n + 3)} \tag{73}$$

where n is the power law exponent. Various additional corrections for capillary flow are described in van Wazer [*42*].

The pressure head ΔP can be obtained two ways: by pressurizing the delivery vessel or by relying on a gravitational hydrostatic head to drive the flow through the capillary. In the latter case, the density of the fluid becomes an important part of the measurement because the rate of flow will depend both on the fluid's viscosity and on the magnitude of ΔP, which now depends on the fluid density, ρ, and on the height of the fluid above the capillary, h ($\Delta P = \rho g h$). The role of the fluid density is taken into account by the kinematic viscosity, defined as

$$\nu = \frac{\eta}{\rho} \tag{74}$$

That is, the kinematic viscosity is equal to the shear viscosity divided by the density. The viscosity obtained from gravity-driven capillary flow is in units of stokes (stoke = P/g/cm^3). The absolute shear viscosity can then be calculated from $\eta = \nu\rho$.

The velocity profile in tube flow is parabolic in shape for Newtonian liquids (as can be proven by integration of Eq 70), with the maximum shear rate at the walls and zero shear rate in the tube center. If non-Newtonian fluids are used, the velocity profile becomes nonparabolic and even more complex. As a result, the viscosity of non-Newtonian materials will vary across the diameter of the tube. Non-Newtonian fluid measurements may be made accurately only if the Weissenberg-Rabinowitsch correction is applied [*106*], which corrects for the variations in viscosity across the capillary arising from the nonuniform shear field.

$$\eta = \eta_a \left[1 - \frac{1}{4} \frac{d(\log \eta_a)}{d(\log \tau_w)} \right]^{-1} \tag{75}$$

where η_a is the uncorrected apparent viscosity.[24] The second term inside the brackets is obtained by calculating the slope of a log-log plot of the measured viscosity versus wall shear stress.

Tube flow is inappropriate for materials with yield behavior. Reviews by Schoff [*97,98*] describe the application of capillary viscometry to coatings.

[24]The "apparent viscosity" is simply the quotient of the apparent (experimentally measured) shear stress and the apparent shear rate. The "true" values of the foregoing, however, may be different from the apparent, where corrections are necessary, say, for flow fields where the shear rate may be varying across the field and must be corrected for non-Newtonian effects.

High-Shear Capillary Rheometry

It has been claimed by some that the measurement of very high shear rate viscosity is not necessary because it may be estimated from moderate-shear data. This is true to an extent, especially if one can obtain an adequate description of the general flow curve by use of one of the flow models containing the high-shear limiting Newtonian viscosity, η_∞ (e.g., the Sisko, Cross, or Carreau models). If a good fit to experimental data can be obtained, the latter models can be extrapolated to predict viscosity beyond the experimental range of shear rate with caution. The power-law-based models should not be used for estimation of high-shear viscosity since they predict unrealistic high-shear behavior (see **Shear-Dependent Viscosity**). However, under the best of circumstances, data should be extrapolated no further than about a decade of shear rate. This means that, in general, shear rates of less than 10^5 s^{-1} can be reached, even by extrapolation methods. It should be pointed out here that the onset of shear thickening (Region IV, Fig. 3) cannot be predicted by extrapolation, yet can cause disastrous consequences in high-shear application processes. For precise comparisons of materials, extrapolation will be unsatisfactory in any case. In fact, several industrial processes involve shear rates of 10^5 to 10^6 s^{-1}. These include airless spray and reverse rollcoating, for example. Performance problems of coatings exposed to such high shear will be difficult to resolve without direct experimental measurement under the appropriate deformation conditions. Such severe conditions of shear can cause a fundamental change in a material, such as gross coagulation of an emulsion, with a possible deleterious effect on rheology and hence on postapplication film formation behavior. It is recommended, therefore, to characterize materials exposed to high-shear processing by high-shear rheometry.

There are some commercial high-shear viscometers which use small-gap bob-in-cup geometry. Problems with this geometry include poor temperature control due to viscous heating and a tendency toward flow-field instabilities. Capillary viscometry has some advantages in both regards. The very short residence time in the capillary at high flow rates minimizes temperature rise, and, for length-to-diameter (L/D) ratios of 50 or greater, entrance effects are negligible and the flow field will be essentially uniform.

By use of short, small-diameter capillaries and high pressures, shear rates of approximately 10^6 s^{-1} are achievable for fluids in the range of viscosities typical of paints. At this writing, we are aware of only three commercial rheometers which may be suitable for high-shear rate measurement of coatings fluids. One is the ACAV High Shear Capillary Rheometer, marketed by ACA Systems Oy, Finland. Another capillary instrument capable of very high-shear measurements is the Paar-Physica HVA-6. The third is the Rheometrics RFX, which uses very narrow-gap annular flow in order to attain high shear rates at lower flow rates (Table 5).

Rank Pulse Shearometer

This instrument is a relatively inexpensive and easy-to-use viscoelastometer. A fixed-frequency acoustic wave pulse is passed through a test sample and the signal detected by a receiving transducer. The propagation velocity v is measured

TABLE 5—Commercial research rheometers and viscometers.

Instrument	Manufacturer/ Vendor[a]	Price Range[b]	Viscosity Range[c] (mPa·s)	Shear Rate Range[c] (s^{-1})	Test Geometry[d]	Temperature Range, °C
ACAV High-Shear Capillary Rheometer	ACA Systems Oy	E	1–55 000	to 10^6	Tube flow	20–90
Bohlin VOR[e]	Bohlin Instruments	E	$0.1–10^{11}$	$10^{-3}–10^4$	CP,PP,CC	−150–350
Bohlin CSM[e]	Bohlin Instruments	E	$0.1–10^8$	$10^{-5}–10^4$	CP,PP,CC	−15–250 RT-400
Brookfield Synchro-Lectric	Brookfield Engineering	A	$1–10^6$	ca. $1–10^2$	CP,CC	RT RT-300[f]
Brookfield CAP2000	Brookfield Engineering	B	50–30 000	150–24 000	CP	5–75
Carri-Med CSL[e]	TA Instruments	E	$0.1–10^9$	$10^{-6}–10^4$	CP,PP,CC	−100–400
Contraves LS40[e]	Mettler	E	$10^{-3}–10^8$	$10^{-4}–260$	CC	0–150
Contraves Rheomat 108E/R	Mettler	C	3–37 800	26–1290	CC	0–80
Contraves Rheomat 115A	Mettler	D	$0.6–10^6$	0.06–10 500	CP,CC	−10–400
Haake CV System[e]	Haake/Fisons	E	$0.1–10^7$	$0.01–10^3$	CC	5–95
Haake M System	Haake/Fisons	E	$0.1–10^8$	1–40 000	CP,PP,CC	−50–300
Haake RS100[e]	Haake/Fisons	E	$0.1–6 \times 10^8$	$10^{-2}–3000$	CP,PP,CC	−50–350
Haake VT500	Haake/Fisons	D	$1–10^7$	4–6000	CP,CC	−30–200
Irvine-Park FNV Falling-Needle Viscometer	Stony Brook Scientific	B	$0.3–10^4$	$10^{-4}–10^3$	Annular flow	−40–150
Paar HVA-6 Capillary Rheometer	Paar-Physica	D	$0.8–10^7$	$10^2–10^6$	Tube flow	−20–150
Physica Viscolab LC-3, LC-10, LC-100	Paar-Physica	C–D	$1–3 \times 10^7$	0.1–50 000	CP,PP,CC	−60–500
Physica Rheolab MC10–MC120[e]	Paar-Physica	D–E	$1–3 \times 10^{12}$	10^{-3}–50 000	CP,PP,CC	−60–500
Vilastic V-E[e]	Bohlin Instruments	D	0.005–5000	0.1–1000	Tube flow	0.4–95
Weissenberg Rheogoniometer[e]	TA Instruments	E	$1–10^{13}$	$10^{-4}–10^4$	CP,PP,CC	−100–500
Wells-Brookfield Cone & Plate	Brookfield Engineering	A	$5–1.5 \times 10^6$[g]	0.6–750	CP	−15–100
Rank Pulse Shearometer[e]	Pen-Kem	C	...	250[h]	Acoustic wave	10–60
Rheometrics DSR[e]	Rheometrics	D–E	$0.1–10^9$	$10^{-5}–10^4$	CP,PP,CC	−40–150 RT-350
Rheometrics RFS II[e]	Rheometrics	E	$1–10^8$	$10^{-2}–10^4$	CP,PP,CC	0–100
Rheometrics RFX	Rheometrics	D	$30–10^6$	$10^{-2}–10^4(\dot{\epsilon})$ $1–10^5(\dot{\gamma})$	Opposed jets annular flow	0–100

[a]See Appendix A for full address.
[b]Price key—A: \$1,000–\$5,000; B: \$5,000–\$10,000; C: \$10,000–\$25,000; D: \$25,000–\$50,000; E: \$50,000–\$100,000.
[c]Ranges cited are approximate and may require purchase of special accessories to achieve.
[d]CP = cone and plate; PP = parallel plate; CC = concentric cylinder (includes couette, bob-and-cup, double-gap concentric cylinder, coni-cylinder, etc.).
[e]Viscoelastic characterization capability.
[f]With Thermosel©.
[g]Full range for Models LV through HB.
[h]Pulse frequency. Small oscillatory strain provides essentially zero-shear measurement.

from the signal transit time and used to calculate the shear elastic modulus according to

$$G' = \rho v^2 \tag{76}$$

The signal wave is of high frequency but very small amplitude (10^{-4} rad), so that weak gels are not disturbed (the induced strain will likely be within the linear viscoelastic regime). Because of the high frequency used, the measured shear modulus corresponds to the plateau modulus, G_∞ (see **Viscoelastic Models**). This gives a useful measure of the gel strength of even weak gels and has an advantage in this regard over instruments which subject the sample to uncontrolled shear upon closure.

APPENDIX

Instrument Manufacturers and Vendors

ACA Systems Oy
Chemical Analysis & Paper Applications
Tekniikantie 12
02150 Espoo, FINLAND
(ATTN: Ilkka Mustonen)

Bohlin Instruments, Inc.
2540 Route 130
Cranbury, NJ 08512

(609) 655-4447

Brookfield Engineering Laboratories, Inc.
240 Cushing Street
Stoughton, MA 02072
(617) 344-4310 or 344-4313

C. W. Brabender Instruments, Inc.
50 E. Wesley Street
P.O. Box 2127
South Hackensack, NJ 07606
(201) 343-8425

BYK-Gardner, Inc.
1100 East-West Highway
Silver Spring, MD 20910
(301) 589-4747
(800) 343-7721

Cannon Instrument Company
P.O. Box 16
2138 High Tech Road
State College, PA 16804-0016
(800) 533-6232

Haake/Fisons, Inc.
53 West Century Road
Paramus, NJ 07652
(201) 265-7865

Kayeness, Inc.
115 Thousand Oaks Blvd.
Suite 101, P.O. Box 709
Morgantown, PA 19543
(215) 286-9396

Mettler Instrument Corporation
Princeton-Hightstown Road
Box 71
Hightstown, NJ 08520-0071
(609) 448-3000

Paar-Physica USA, Inc.
400 Randal Way B-207
Spring, TX 77388
(713) 350-3576

Pen Kem, Inc.
341 Adams Street
Bedford Hills, NY 10507
(914) 241-4777

Rheometrics, Inc.
One Possumtown Road
Piscataway, NJ 08854
(201) 560-8550

Sheen Instruments Ltd.
Sheendale Road
Richmond, Surrey
England TW9 2JL

Stony Brook Scientific
914 Fillmore Rd.
Norristown, PA 19403
(215) 584-9632

TA Instruments, Inc.
109 Lukens Drive
New Castle, DE 19720
(302) 427-4000

Thomas Scientific
99 High Hill Road
P.O. Box 99
Swedesboro, NJ 08085-0099
(609) 467-2000
(800) 345-2100

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34

Surface Energetics

by Gordon P. Bierwagen[1]

NOMENCLATURE

- a Integration limit, distance from surface into bulk of material, Eqs 3 and 6
- A Surface area
- b Variable in Eq 18, the difference in maximum and minimum diameters in elliptical orifice
- c Surfactant concentration
- c_i Concentration of species i
- c_{i0} Concentration of species i in the bulk
- D Diffusion coefficient
- $\mathscr{E}$ Surface elasticity
- f Correction factor in Eq 15
- g Acceleration of gravity
- G Gibbs free energy
- h Variable defined in Eq 9
- h Height in capillary rise measurements
- i Index identifying species i
- k Wave number = $2\pi/\lambda$ (λ = wavelength, see below)
- l Subscript indicating liquid phase
- l Length of capillary pore path in Eq 23
- $\mathbf{n}$ Normal vector to surface, Eq 3
- n Exponent in Eq 4
- n Most probable number of drops from breakup of charged drop, Eq 31
- n_i Number of moles of component i, Eq 2
- 0 Subscript indicating zeroth or bulk phase, or reference value
- p Pressure
- $\mathbf{p}$ Pressure tensor in the bulk phase, Eq 3
- $\mathbf{p}^T$ Tangential pressure tensor, Eq 3
- $\mathscr{P}$ Perimeter length
- Q Liquid flux, volume/second
- q Charge on drop
- r Variable in Eq 18, sum of maximum and minimum radii in elliptical orifice
- r Radius
- R Ring radius in Du Nouy ring surface tension measurement
- R_1, R_2 Principal radii of curvature
- s Subscript indicating solid phase
- T Temperature
- T_c Critical temperature
- x Distance from surface in Eq 6
- ν Index indicating vapor phase, Eq 10
- v Velocity
- V Volume
- W Weight
- γ Liquid surface tension
- Γ, Γ_i Surface excess concentration, of ith species
- δ_f Final film thickness in dip coating
- Δ Difference
- ϵ Dielectric constant
- η Viscosity
- λ Wavelength
- μ_i Chemical potential of species i
- π 3.141 59
- Θ Contact angle
- ρ Density

INTRODUCTION

SURFACES ACT AND PERFORM differently from bulk materials because they have two distinct properties that are not true of bulk materials. First, because of unbalanced forces on molecules or atoms at a surface as compared to the bulk, those in the surface have an excess free energy [*1*] (i.e., they are in a higher state of potential energy). This excess energy per unit area is the thermodynamic cost of forming a new surface and has the units of energy/area, or force/length. These latter units are those of tension, and the surface excess free energy is often known as surface tension and can be measured for liquids as such. (A more detailed discussion of this excess free energy identified with a surface, including the thermodynamic definition of surface tension, is given below.) Second, there is a preferred direction normal to the surface that can be defined in the mechanical definition [*2*] of surface tension. This directional effect of surfaces can be observed in molecular directionality in adsorption phenomena, surface area minimization by surface tension effects, and molecular ordering in Langmuir-Blodgett films deposited from ordered mono-molecular layers (monolayers).

Surfaces occur only when there is an energetic cost to creating an interface between two dissimilar materials or phases. Thus, there are no stable interfaces between gases, between supercritical fluids, nor among phases in a material above its critical point. However, surfaces can occur between gas and liquid (g/l), liquid and liquid (l/l), gas and solid (g/s), liquid and solid (l/s), and between solid and solid (s/s). An example of a g/l interface is the surface of a pool of water, and so forth. Liquid surface energy phenomena can be analyzed directly by equilibrium thermodynamics because a liquid

[1]Professor of Polymers and Coatings, Department of Polymers and Coatings, North Dakota State University, Fargo, ND 58105.

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surface cannot support a stress. For a solid, surface energy and surface stress must both be considered in analyzing the properties of an interface, since the past history of the solid will affect the properties of a solid surface [3]. Even though this is well known, there has not been as much concern given to the surface history of solids in considering their surface properties as often necessary.

Surface effects relative to bulk properties become more important as the surface area to volume ratio for materials becomes larger. In the simplest case, a sphere, this ratio is given by

$$\frac{A}{V} = \left[\frac{4\pi r^2}{\frac{4}{3}\pi r^3}\right] = \frac{3}{r} \tag{1}$$

Surface effects thus increase in importance as the size of the object being considered becomes smaller. Statistical thermodynamics and molecular dynamics considerations indicate that the range of the range of surface effects as 2 to 5 molecular diameters [4]. An interesting feature of this type of analysis of surface effects and their ranges is that the distance of propagation of surface effects into the bulk from a polymer adsorbed at an interface can be quite large in atomic dimensions. In effect, the interface is a site of pinning one end of the polymer, taking away one of its degrees of freedom of motion, and thus making the interface a location of a layer of polymer of different thermomechanical properties than the rest of the polymer. This is exceptionally important when analyzing the adhesion of polymeric films to bulk substrates. The strength of the adhesive bond can be influenced by these directionality effects and can be even more important if the substrate is a plastic (polymer), where the ordering effects propagate on both sides of the interface. The directionality and ordering of surrounding polymeric bulk media by an interface can extend unexpectedly large distances. Many of the properties of self-ordering systems have these effects as their origin. This will be commented upon further in the discussion of surface effects in pigment dispersion and emulsions.

All who deal with coatings must realize that surface effects are very important in all stages of coatings preparation, application, and utilization. Coatings are thin films with a high surface-to-volume ratio. Pigments have large surface-to-volume ratios, and their surfaces are often chemically reactive or catalyze reactions [5]. Latex polymers also occur in fine particulate form, and their use and stability depend on surface-dominated effects. Foaming, cratering, and other defects in coatings come about through surface-mediated events [6]. Wetting and coverage of substrates by coatings and the adhesion of coatings to these same substrates are also strongly affected by surface effects. Adsorption at surfaces of particulate materials in a coating, be they pigments or polymer particles, is controlled by the energetics of the interface between the particles and the suspending liquid.

SURFACE THERMODYNAMICS—BASICS

Liquid Surfaces

To understand surface energetics in coatings, one must first understand the basics of the thermodynamics of surfaces and interfaces. The definition of the Gibbs free energy is modified when the system under consideration contains a surface. The defining equation for liquids is

$$dG = -SdT + Vdp + \Sigma_i \mu_i dn_i + \gamma dA \tag{2}$$

where G, T, S, V, p, μ_i and n_i are the thermodynamic quantities Gibbs free energy. Temperature, entropy, volume, pressure, chemical potential of component i, and the number of moles of component i, respectively, and γ and A are the surface tension and surface area. The other equations of thermodynamics can be similarly modified. As can be seen, the energetic cost of expanding a liquid surface is the γdA term. As pointed out above, this use of γ is valid only for liquid interfaces. Another equation for γ is the mechanical definition of Ref 2, also discussed by Adamson [1] and reviewed by Burshtein [7] and Navascues [8] as

$$\gamma = \int_{-a}^{+a} (\mathbf{p} - \mathbf{p}^T)\, d\mathbf{n} \tag{3}$$

where $+a$ and $-a$ are distances in either direction of the surface such that molecules at these positions are in the bulk phases, $\mathbf{p}$ and $\mathbf{p}^T$ are the bulk pressure and the tangential pressure tensors, respectively, and $\mathbf{n}$ is the normal vector to the surface. This is shown schematically in Fig. 1. The direction of $\mathbf{n}$ is the preferred direction of a surface referred to above. Even if it is not commonly included in introductory discussions of surface phenomena, it is important to consider Eq 3 when considering the thermodynamics of surfaces because it is the relationship between the bulk mechanical properties of the system and the almost "distincontinuous" behavior of the system properties at an interface. This expression describes the *directionality* that an interface possesses and is very crucial to modern theories of capillarity [9].

In general, the surface tension, γ, of pure liquids decreases with increasing temperature. An approximate form of this temperature dependence is [10]

$$\gamma = \gamma^0 \left(1 - \frac{T}{T_c}\right)^n \tag{4}$$

where γ^0 is the surface tension at $T = 0$, T_c is the critical temperature of the material, and n is an empirical exponent, ~11/9 for organic liquids.

The other important thermodynamic relation for surfaces is the Gibbs equation. In multicomponent systems, one must consider the effects of materials absorbing at the interface. When these are properly taken into account, the Gibbs equation (at constant T and p) results

$$d\gamma = -\Sigma_i \Gamma_i d\mu_i \tag{5}$$

where Γ_i is the surface excess concentration value for component i [11]. This equation gives the relationship between the surface tension of a fluid interface and the amounts of surface active materials (hereafter referred to as surfactants) in the solution (component i). The surface excess concentration Γ_i is the difference between the actual and bulk concentrations, c_i and c_{i0}, of component i and can be calculated in a manner analogous to Eq 3 as

$$\Gamma_i = \int_{-a}^{+a} (c_i - c_{i0})\, dx \tag{6}$$

where x is again the direction normal to the interface and $+a$ and $-a$ are locations equidistant from the interface in the bulk of the material. This is shown schematically for a single surfactant in Fig. 2. In adsorption of materials to an interface,

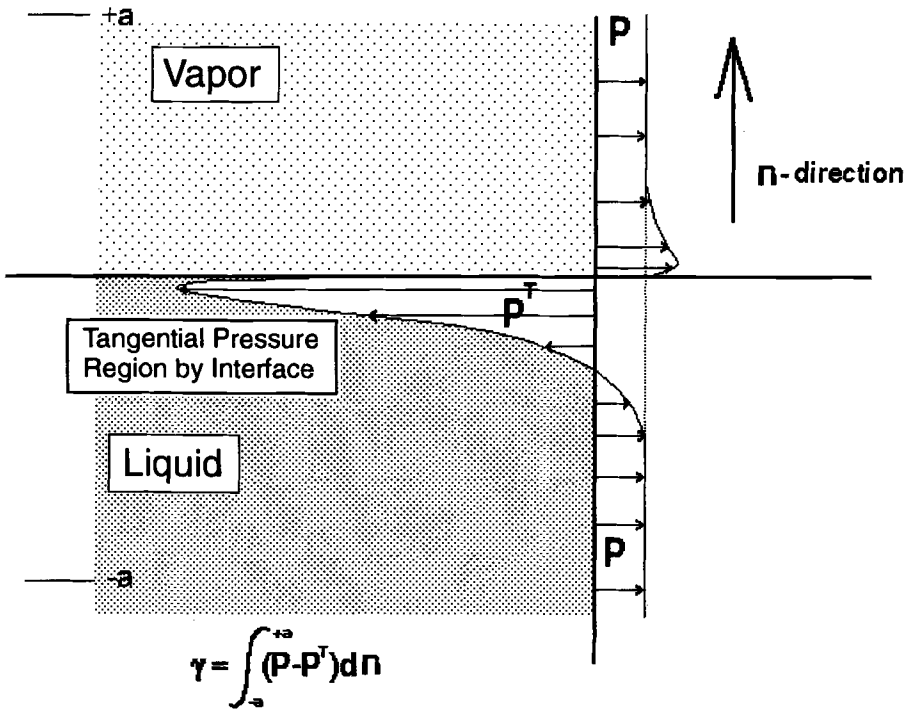

FIG. 1–Schematic of local pressure changes at surface giving surface tension.

the local concentration in the neighborhood of the interface can be much larger (by factors of up to 10^8 or larger—see Ref *1*, Chapter III for further details) than that in the bulk. The net energy of the system is minimized by the surfactant molecules adsorbing and orienting at the interface to reduce interactions between unlike molecular components. The terms often used to describe the compositional differences in surfactants are polar/nonpolar or hydrophobic/hydrophilic. Materials that act as surfactants are those that have a distinct difference between different parts of their molecules, the

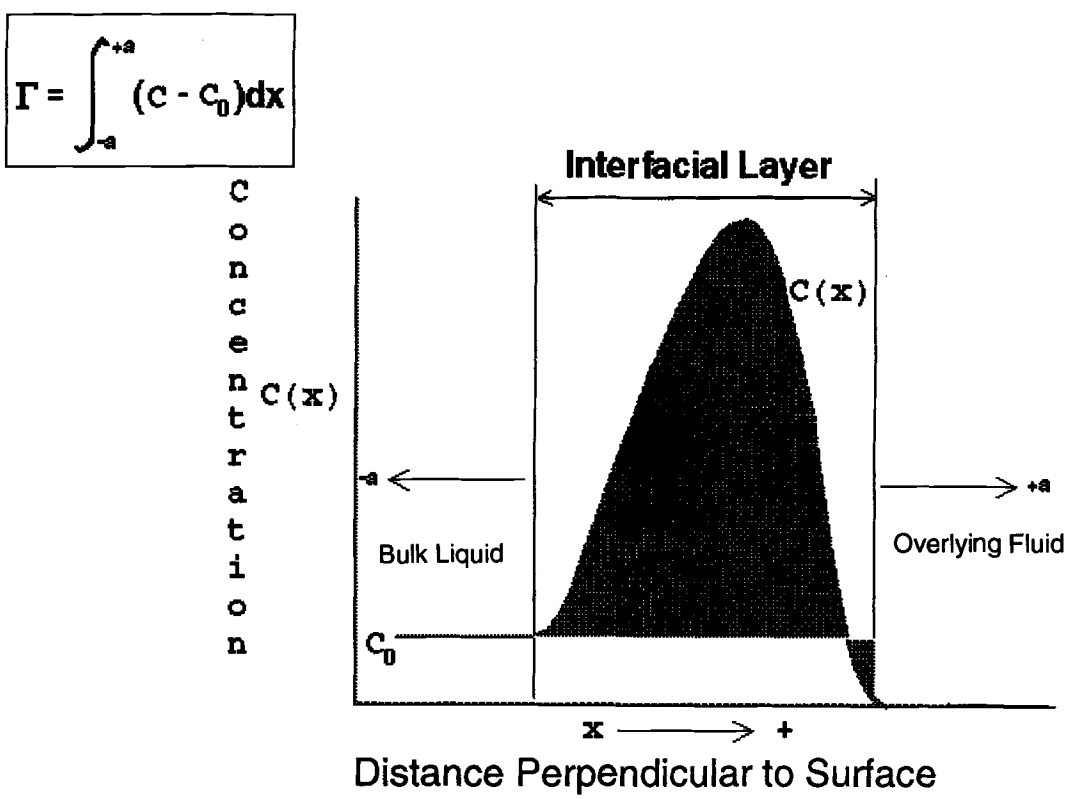

FIG. 2–Schematic of surface excess concentration as calculated as difference for bulk concentration.

classic example being soaps, with an alkyl nonpolar group and a [carboxylate + metal ion] polar group.

In concentrated systems of surface-active materials, especially those of low inherent solubility in the liquid phase, at a certain concentration the addition of further surfactant no longer depresses the surface tension, as the surface is saturated, and the molecules of the surfactant begin to form self-ordered structures in the bulk liquid called micelles [*12*]. Micelles are aggregates of surfactant molecules that form in solution to minimize the total system energy. In water they orient with the hydrophobic portion of the molecule directed toward the interior of the micelle, and in nonaqueous systems they have the polar end in the interior. At the concentration of surfactant that micelles just begin to form, many of the solution properties also undergo rapid change, and this breakpoint in surfactant solution properties is known as the critical micelle concentration (CMC) (Fig. 3). The CMC is a unique concentration for a surfactant/solvent combination at a specified temperature. The book by Rosen [*13*] gives an expanded discussion of surfactant behavior, and Tanford's book [*14*] gives an expanded description of micellar behavior in aqueous systems. These texts also describe the complex aggregates that form in surfactant/solvent mixtures, including membrane-like structures and liquid crystals.

As Gibbs first noted, the presence of a material adsorbing preferentially at an interface imparts an elasticity to the surface, as it will tend to resist expansion and contraction. This surface elasticity is given by

$$\mathscr{E} = -\frac{d\gamma}{d\ln A} = -\frac{d\gamma}{d\ln\Gamma} \tag{7}$$

where A is the surface area. This elasticity is the resistance to disturbance of a film by the presence of a surfactant. The effects of this surface elasticity have been reviewed with respect to its effects in liquid films and liquid threads [*15*]. Surface elasticity measurements have been used to characterize the properties of monomolecular layers at surfaces [*16*]. If there are diffusional effects due to soluble surfactants (see below, "Dynamic Properties of Surfaces"), they will reduce the surface elasticity, effectively short circuiting the surface tension changes by surface replenishment [*17–19*]. In these cases, Eq 7 should be modified to read

$$\mathscr{E} = \frac{-(d\gamma/d\ln\Gamma)}{[1 + (h/2)(dc/d\Gamma)]} \tag{8}$$

where c is the surfactant concentration and h is given by the relationship

$$h = 2\sqrt{\frac{D}{\omega}} \tag{9}$$

where D is the surfactant diffusion coefficient, and ω is the frequency of the surface motion [*18*]. Surface elasticity effects are a major consideration in foam stability [*20*] and in coating application processes [*21*], where there are rapid surface area changes and creation of new surfaces.

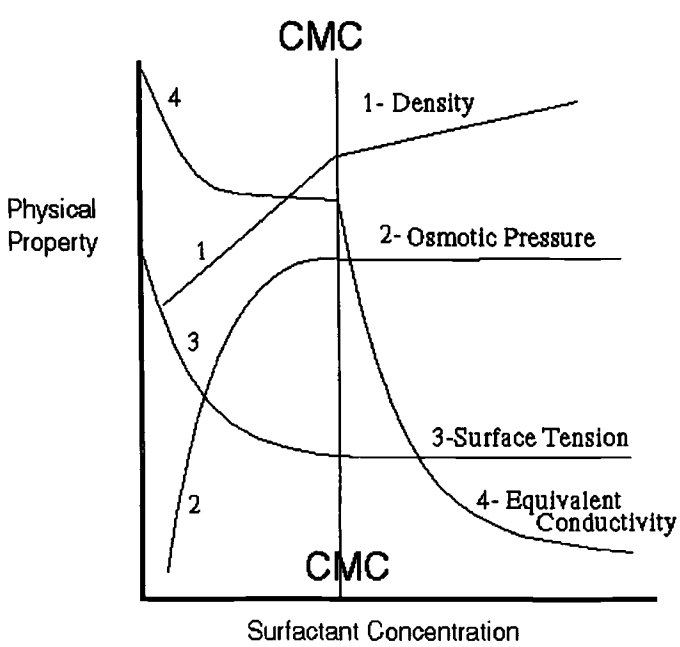

FIG. 3–Schematic of physical property changes in surfactant solution at critical micelle concentration (CMC).

Liquid/Solid Interfaces: Wetting and Contact Angles

When a liquid solution is in contact with a bulk solid, the Young equation holds true as

$$\gamma_{sl} - \gamma_{sv} + \gamma_{lv}\cos\Theta = 0 \tag{10}$$

where γ_{sl}, γ_{sv}, and γ_{lv} are the solid/liquid, solid/vapor, and liquid/vapor surface tensions, respectively, and Θ is the contact angle formed between the liquid and solid [*9,22*]. This is shown in Fig. 4 and discussed extensively in the references given above. The contact angle between a liquid and a solid is in some ways a measure of the difference in surface energies of the solid and liquid. If a liquid "wets" a solid, the contact angle is zero, and the liquid spreads spontaneously over the surface of the solid, displacing air in contact with the solid surface. If the contact angle is greater than zero, a liquid will not wet and spread on a solid. An extreme example of this is found with Teflon™, which is of such a low surface energy that it is wet by few pure liquids or solutions. In general, pure

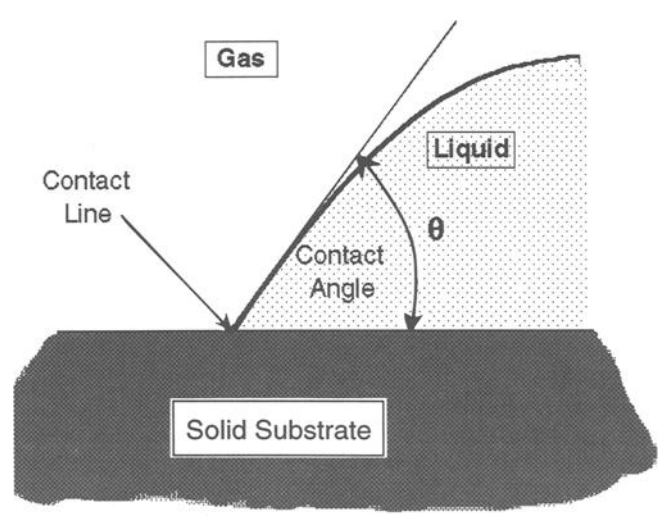

FIG. 4–Schematic of contact angle in G/L/S system.

hydrocarbon and fluorocarbon interfaces that are nonpolar in nature have very low surface energies and are difficult to wet, while polar materials such as metals and metal oxides have high surface energies and are easily wet. Oils or other impurities on the surface of a polar substrate will cause the material to act as a low surface energy solid, making it difficult to wet. There is extensive qualitative discussion in the literature concerning polar and nonpolar contributions to surface energetics, much of it of value only in a qualitative sense as a guide to interpreting the wetting behavior of pure liquids. Good and Fowkes have both published extensively in this area (see Refs *1* and *23* for a more complete listing of these citations), and the literature is full of equations of arguable theoretical value invoking empirical relations between composition and surface energetics, including acid-base interactions [*23*]. In coatings application, it is very crucial to have the liquid coating wet the substrate. Substrate cleaning and the use of surfactants to depress the liquid coating surface tension and reduce the contact angle to zero are two of the most common steps to achieve this. It is essential to have this wetting of the substrate to obtain good adhesion of the coating to the substrate, hence the importance of proper surface preparation for coatings use.

Rough surfaces tend to have lower contact angles than smooth surfaces of the same composition [*24*]. This is why sanding or other surface roughening will give better wetting of a material by a coating. There is also often a difference in the contact angle measured by an advancing drop and a receding drop, the advancing angle being the larger. This is often due to surface roughness, causing a hysteresis in the contact angle [*25*]. Surface compositional differences and their scale have also been shown to give hysteresis, both by themselves and together with surface roughness [*26*]. These literature references, plus many others (see Ref *1* for a more complete discussion), indicate the difficulties in obtaining completely unambiguous contact angle measurements, especially when considering both advancing and receding drops on solid surfaces. Zisman and coworkers have also shown that there is a "critical surface tension" characteristic of a given surface [*27*]. This is determined by plotting the cosine of the contact angle Θ versus surface tension and extrapolating to $\cos \Theta = 1$ (zero contact angle) and determining the surface tension at this value. This is often used to determine the relative surface energy of a solid and the surface tension required of a wetting liquid for that surface. Pure liquids can be used as test liquids for the measurement of critical surface tension, or surfactant solutions can be utilized [*13,28*]. Some precautions need to be taken on the choice of test liquids as the polarity of the test liquid may influence measurements and thus the extrapolation procedure used to estimate the critical surface tension (see Ref *1* for further details).

Exposure to exterior weathering has been noted to decrease contact angles of organic coatings and other polymeric films [*29*]. Similar effects are noted when these surfaces are modified by corona or flame treatment, and these treatments are often used to give wetting and adhesion of coatings to hard-to-wet plastic substrates such as polyethylene and polypropylene. In addition to these surface treatments, it has been found that certain chlorinated olefinic polymers improve the wetting and adhesion of coatings to polyolefin plastics [*30*].

DYNAMIC PROPERTIES OF LIQUID SURFACES

When fresh surfaces are formed in a liquid solution, such as in coatings application processes, manufacture, etc., the surface tension and composition of the fresh surface of a solution will be different from the equilibrium value. At the time of new surface creation, the surface tension of the liquid will be nearly equal to the surface tension of the pure solvent at the instant of the surface formation. The surface tension then decreases as the surfactant in the solution diffuses to the interface. The dynamics of the diffusion from bulk to interface, or vice versa in the case of surface compression, has been well studied, initially by Ward and Tordai [*31*] and later by Sutherland [*32*], Hansen [*33*], Joos [*34*], and others. There are also possible complicating effects if the adsorbing material is polymeric, for which case additional time-dependent changes in the surface tension may occur as the polymer molecules relax to their equilibrium conformation at the surface, or if there is an energy barrier to adsorption of the material [*35,36*]. Special methods have been developed to measure dynamic surface tension, and these are discussed below, along with static surface tension measurement methods. It is especially important to consider and eliminate dynamic surface tension effects if one is trying to measure the equilibrium value of $\gamma[\gamma(t)$ for $t \rightarrow \infty]$, meaning for example, a Wilhelmy plate rather than a Du Nuoy ring is the appropriate measurement for systems that are other than pure liquids. These dynamic effects are especially important in coating application processes and all coating operations that generate fresh surfaces [*37*]. There are also dynamic effects in the wetting of surfaces that must be considered for coating application operations. The first is the dynamics of wetting in thin film spreading as discussed by de Gennes [*38*]; the other is the dynamics of contact angles on moving substrates [*39*].

MEASUREMENT OF THE SURFACE TENSION OF LIQUIDS

Introduction

There are many ways of measuring surface tension, but in essence, they are all related to two effects of capillarity. The first effect is the excess pressure due to surface tension at a curved interface. This is described by the Young-Laplace equation as

$$\Delta p = \gamma(1/R_1 + 1/R_2) \tag{11}$$

where Δp is the excess pressure due to the curved interface, and R_1 and R_2 are the two principal radii of curvature of the interface. In the case of a sphere of radius r, where the radii of curvature are both equal to r, this equation reduces to

$$\Delta p = 2\gamma/r \tag{12}$$

The other capillary effect is that the surface tension of a liquid exerts a force on a solid body immersed in it equal to the surface tension times the perimeter of the body times the contact angle the liquid makes with the solid. If one is using a balance, one can write

$$\Delta W = \mathcal{P}\gamma \cos \Theta \tag{13}$$

where $\mathcal{P}$ is the perimeter and Θ is the contact angle, and ΔW is the extra force on the solid body due to surface tension. These two effects yield, together with various modifications of geometry, etc., many methods to measure static and dynamic surface tension. The most widely used methods are described below.

In all measurements of surface tension, the cleanliness of all apparatus and the purity of all materials is of utmost importance. Organic impurities in aqueous systems will have drastic effects in reducing the surface tension values measured. The concentration levels necessary to alter surface tension measurements are as little as 10^{-8} M. Trace amounts of impurities on solid apparatus surfaces can alter contact angles and, as will be shown, the measured surface tension values. All water used in surface tension measurements should be at least double distilled, and often the presence of a strong oxidizing agent in one step of the distillation ensures that trace surfactants are removed. The water should be used fresh, as surface active impurities can be leached from glass and plastic containers. The same holds true for all solvents used in surface characterization studies.

Static Surface Tension Measurements

There is a group of surface tension measurement methods that apply well only to a static system. These methods must thus be used on systems where there is no formation of fresh surfaces, or with pure liquid.

Capillary Rise

There will be a pressure on a liquid in a small capillary tube relative to the pressure on a large vessel of the liquid. Using Eq 12 and allowing for the contact angle between the liquid and the capillary, we have at equilibrium between the force of gravity and the capillary pressure

$$\Delta\rho g h = \frac{2\gamma \cos \Theta}{r} \tag{14}$$

where $\Delta\rho$ is the density difference between the liquid and air, g is the acceleration of gravity, h is the height of the capillary rise, and the rest of the terms are defined above. This equation allows one to measure the surface tension from a simple measurement of the height of the rise of the liquid in a capillary of known radius and contact angle with the test liquid. This method is shown schematically in Fig. 5.

Drop Weight

The weight of a drop when it is formed slowly is the weight just to exceed the force of surface tension times the radius of the capillary tip from which it is formed, with a correction factor required for the formation of small satellite drops. Thus, one has

$$W = 2\pi\gamma r f \tag{15}$$

where W is the weight of the drop and f is the correction factor which is discussed in Adamson [*1*]. This method is simple to use and accurate if precautions are taken for cleanliness and very slow flow rates of the liquid in the formation of drops. The method is shown schematically in Fig. 6.

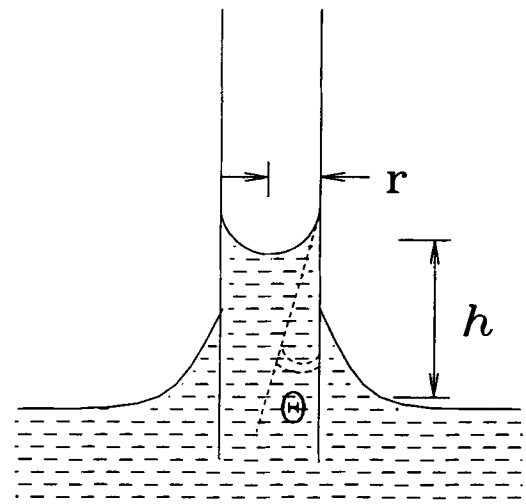

FIG. 5–Schematic of capillary rise method of measuring surface tension.

Du Nuoy Ring

Applying Eq 13 to the case where the object is a ring being pulled from the surface of a liquid, one has

$$W = W_{\text{ring}} + 4\pi\gamma R \tag{16}$$

where W is the total weight sensed by a balance, W_{ring} is the ring weight, and R is the ring radius as shown in Fig. 7. However, this formula requires correction to be accurate and holds only for a zero contact angle between the ring and test

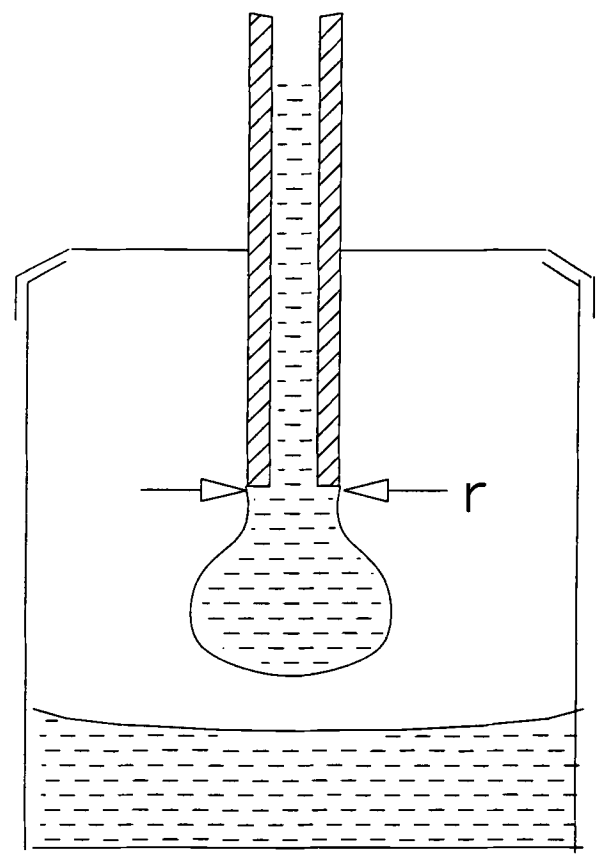

FIG. 6–Schematic of drop weight method of measuring surface tension.

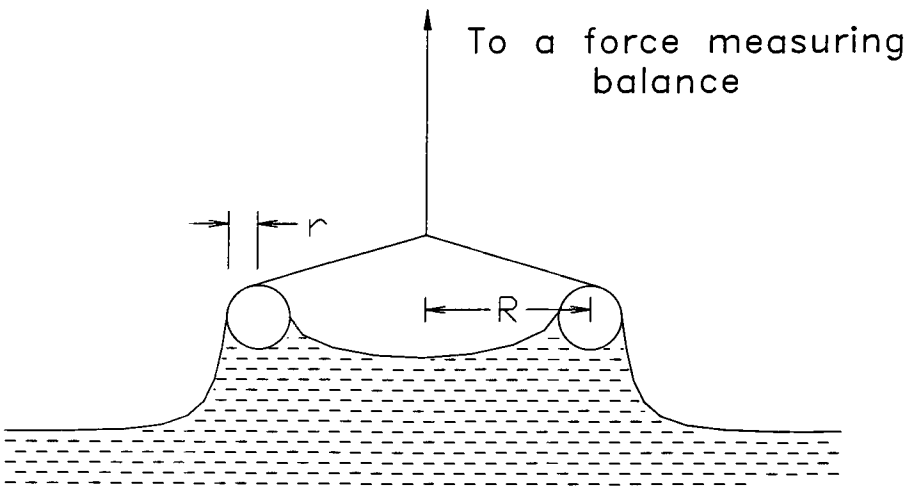

FIG. 7–Schematic of Du Nuoy ring method of measuring surface tension.

liquid. Again, see Adamson [*1*] for further details. The force measured by the balance is that force just at detachment of the ring and so involves motion of the sensor; the method is thus not an appropriate technique to use in studying solutions.

Wilhelmy Plate

If one uses a thin plate instead of a ring and measures the force exerted on the plate just touching the surface of a liquid, one has

$$W = W_{\text{plate}} + \gamma\mathcal{P} \tag{17}$$

where $\mathcal{P}$ is the perimeter of the plate. If the liquid does not perfectly wet the plate, the expression

$$W = W_{\text{plate}} + \gamma\mathcal{P}\cos\Theta \tag{17a}$$

must be used as illustrated in Fig. 8. The perimeter of the plate may be determined in practice as an experimental constant from γ measurements with liquids of known surface tension. Again cleanliness is most crucial, and a roughened platinum plate cleaned in a Bunsen burner flame is often used to give a clean plate that is wet by most liquids. As there is no motion of the plate in the measurement, this method can be used to measure dynamic as well as static values of γ. This technique may be used as well with a rod [*40*] or cone [*41*] instead of a plate and may also be used to measure the contact angle of a liquid of known surface tension against a specific plate, fiber, or cone-shaped substrate (see later in this chapter under **CONTACT ANGLE MEASUREMENTS**). Also, the method does not need corrections as with the drop weight or the Du Nuoy ring methods.

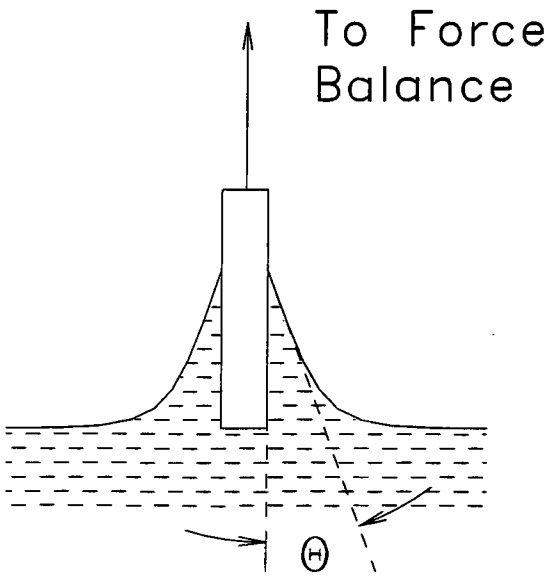

FIG. 8–Schematic of Wilhelmy plate method of measuring surface tension.

Sessile or Pendant Drop Shape Methods

If the shape of a sessile or pendant drop is measured photographically or a digitizing camera, a solution of Eq 11 for the specific shape of the drop in the presence of a gravitational field can be used with the measurements of the drop profile to back calculate the surface tension of the drop. Figure 9 gives a schematic of the method. This method works well at liquid-air or liquid-liquid interfaces and can also be used to make dynamic measurements if the camera response is continuous and rapid [*42*]. A variation of the drop-shape method of measurement is used wherein the drop is deformed by a centrifugal field or an electric field. The former, the spinning drop shape method, allows very small interfacial tensions to be measured between two liquids [*43*].

Maximum Bubble Pressure Methods

If one forms a bubble within a liquid by forcing a gas out the end of a capillary, the maximum pressure on the bubble can be used to measure surface tension by Eq 12. This measurement procedure is illustrated in Fig. 10. However, the measurement must be corrected for the nonspherical shape of the bubble. With rapid formation of the bubbles and accurate differential pressure measurement, the technique may be used to make dynamic measurements [*44*]. If capillaries of two different radii are used simultaneously and the pressure difference between the bubbles formed at the two capillaries is measured, a rapid, accurate measurement of surface tension can be made and has been used as a process monitor in emulsion polymerization [*45*]. This is known as the differential bubble pressure method and is illustrated in Fig. 11.

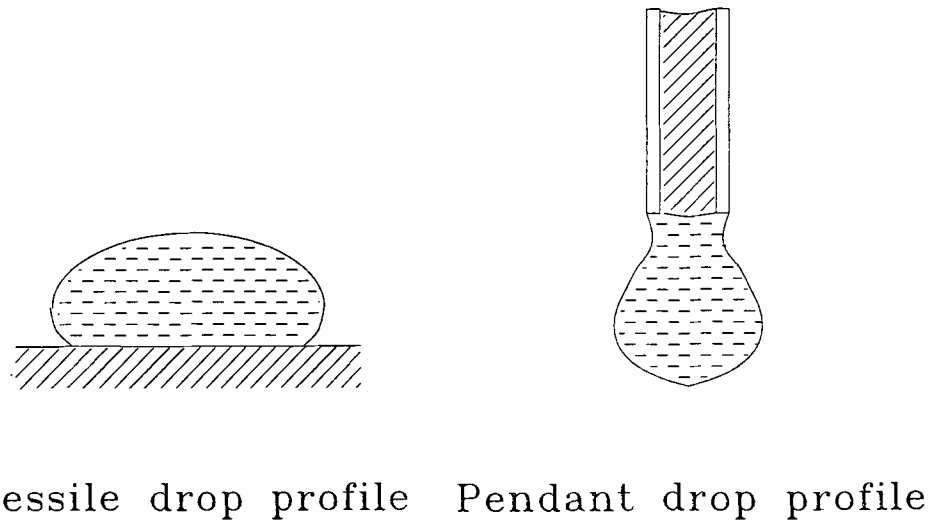

FIG. 9–Schematic of sessile and pendant drop methods of measuring surface tension.

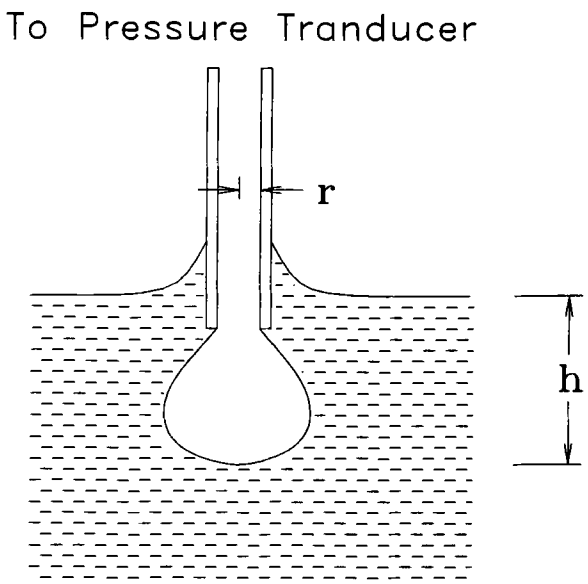

FIG. 10–Schematic of maximum bubble pressure method of measuring surface tension.

Dynamic Surface Tension Methods

If one is concerned with surface tension effects that occur in freshly formed surfaces, in flow systems, or in polymer solutions where the time for equilibrium may be quite long, one must consider methods that properly measure dynamic surface tension. As mentioned above, bubble pressure and drop-shape methods as well as the Wilhelmy plate method can be used for static as well as dynamic γ measurements. These methods are appropriate only for relatively slow changes in γ, but we discuss them briefly below and provide literature references that discuss their use in characterizing $\gamma(t)$ effects. There are techniques to measure γ that have been developed specifically for short-time scales and fresh, rapidly changing surfaces.

Oscillating Jet

If a liquid leaves as a jet through an elliptical orifice, it is mechanically unstable and will begin to oscillate about a circular shape, as shown in Fig. 12, eventually breaking up into droplets. The oscillations are periodic, and measurement of their wavelength can be used to determine γ as given by

$$\gamma_{\text{app}} = \frac{4\rho v^2 \left(1 + \dfrac{37b^2}{24r^2}\right)}{6r\lambda^2 \left(1 + \dfrac{5\pi^2 r^2}{3\lambda^2}\right)} \tag{18}$$

where ρ is the liquid density, v is the velocity of the jet, λ is the wavelength of the oscillation, r is the sum of the minimum and maximum diameters, and b is their difference [*1*]. This dynamic measurement of γ has been considered by Vijian and Ponter [*46*], who give references to the earlier work of Rayleigh, Bohr, Sutherland, Hansen, and others.

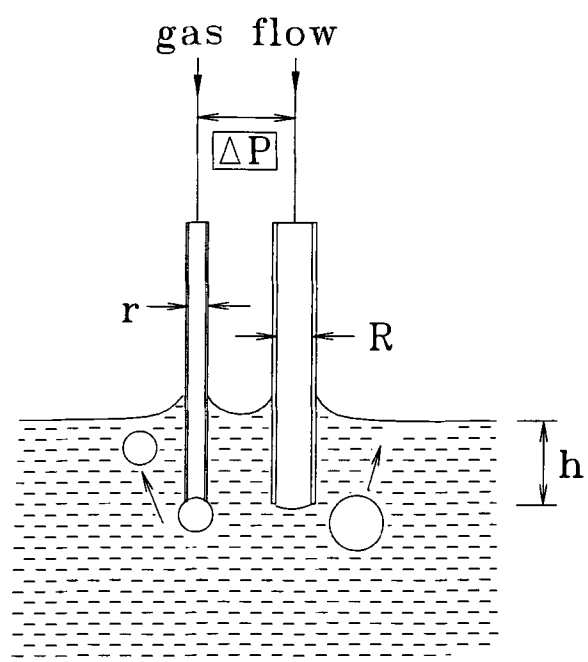

FIG. 11–Schematic of differential bubble pressure method of measuring surface tension.

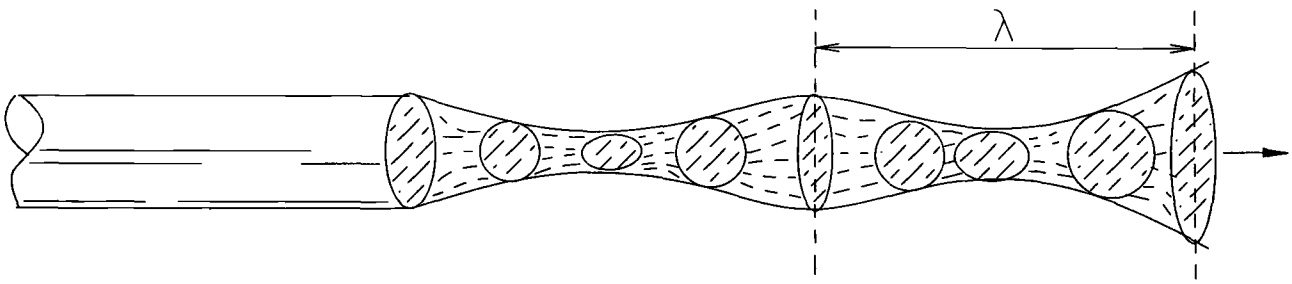

FIG. 12–Schematic of oscillating jet method of measuring surface tension.

Falling Curtain

In an analysis of curtain coating, Brown [*47*] observed that the angle Θ in the falling curtain formed by the break around a small, nonwettable obstacle could be used to measure surface tension as

$$\sin \Theta = \frac{2\gamma}{Qu} \tag{19}$$

where Q is the mass flow rate per unit orifice slit length in the curtain and u is the velocity of the liquid. This can enable one to calculate the dynamic surface tension in the falling film at the point where the obstacle intersects the falling curtain if the velocity u is greater than the "bursting velocity" of the falling sheet. A schematic of this method is given in Fig. 13. This has been considered further by Van Havenburgh and Joos [*48*]. Antoniades et al. [*49*] reconsidered the work of Brown and suggest that Eq 19, when derived correctly, should be written as

$$\sin^2 \Theta = \frac{2\gamma}{Qu} \tag{19a}$$

and give experimental evidence for this corrected equation.

Capillary Waves

The properties of capillary waves, small wavelength waves on the surface of a liquid with the dominant restoring force being surface tension, can be studied to provide a measurement of surface tension, surface elasticity, and other dynamic surface properties. For clean surfaces of an inviscid liquid, Kelvin [*50*] determined that on a liquid of density ρ, waves of frequency ω, and wave number k, the surface tension is given for small wavelengths

$$\gamma = \frac{\rho\omega^2}{k^3} \tag{20}$$

The situation for interfaces in real systems, viscous liquids with surfactants present, has been studied in detail [*8,9*], and the use of mechanically generated capillary waves for studying interfaces has been reviewed by Hansen and Ahmad [*51*]. The capillary waves generated by temperature fluctuations at a surface can be measured by laser-light scattering techniques, and these data can be used to generate very accurate values of surface and interfacial tensions [*52*]. Capillary wave studies can be used to study the time dependence of γ in some detail and are probably the most accurate and complete of the methods for measuring all dynamic surface properties.

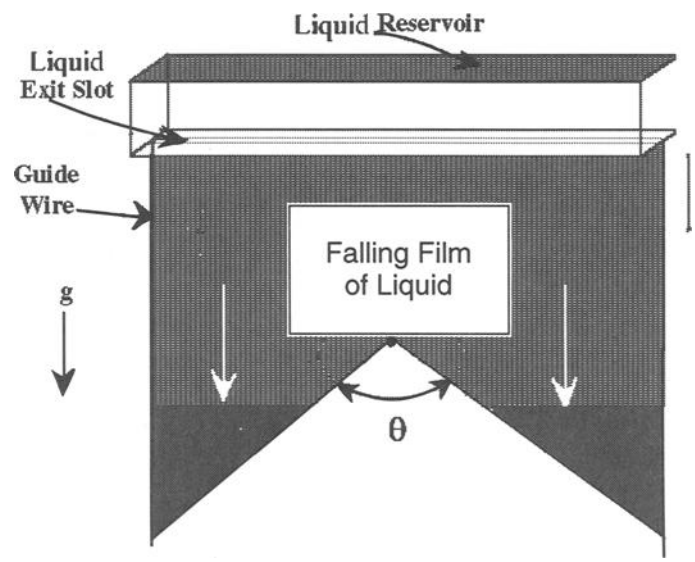

FIG. 13–Schematic of falling film method of measuring surface tension.

The Falling Meniscus Method

The measurement of the height of a column of liquid in a tube with a small opening on top can be used to measure the dynamic surface tension of aqueous systems. The height measurement versus time may be analyzed to calculate the surface tension as a function of time. This is discussed in further detail, together with a full description of the experimental apparatus and analytical equations, by Defay and Hommeln [*53*].

Modified Static Surface Tension Measurements

Maximum Bubble Pressure—If one can monitor the time response of pressure to the time-dependent surface tension, one can use the maximum bubble pressure technique described above to measure dynamic surface tension [*44*]. The equipment required for such measurements is the same as the static maximum bubble technique plus instrumentation for time-dependent measurement of the bubble pressure. Various authors have examined the theoretical and experimental aspects of this method [*34,54*].

Wilhelmy Plate—If a time-recording balance is used to monitor the force of surface tension pulling on the immersed plate, the Wilhelmy plate technique can be used for characterizing dynamic surface tension. As discussed above, the method is not useful for short times, but for slowly varying $\gamma(t)$ values. The method is used considerably with Langmuir

film balances and has been applied to various other problems [*55*].

Other Methods—If a sensing technique that can be time resolved is coupled to a specific static surface tension measurement, $\gamma(t)$ data can be acquired. Reference *42* discusses this for drop-shape methods, and Jho and Burke [*56*] present a modification of the drop weight technique for $\gamma(t)$ characterization.

CONTACT ANGLE MEASUREMENTS

Optical Measurement Methods

Contact angles are often measured by some form of optical measurement technique, either directly by a contact angle goniometer, by a measurement on a photograph of a drop shape, or digitally on a video image of the drop. A diagram of a contact angle goniometer is given in Fig. 14. This measurement often is done with the aid of a microscope. [*57*]. One can also calculate the contact angle from the dimensions of a drip on a solid surface. The corrections and information given in sessile drop, etc., measurement descriptions inherently contain information on the drop profiles, including the contact angle [*38,39*]. A more complete discussion of contact angle measurements is given by Neuman and Good [*58*], and Adamson [*1*] also surveys these measurements. Sell and Renzow [*59*] have reviewed the application of contact angle studies to pigments and give comments on the measurement of contact angles in pigments. The relation of wetting and the thermodynamics of liquid-solid interfaces to adhesion are discussed in some detail in the monograph edited by Lee [*60*].

Wilhelmy Plate Method

Using the solid substrate material to be coated as the plate and a liquid of known surface tension as the test liquid, the Wilhelmy Plate method (Eq 17) can be modified to give

$$\cos \Theta = \Delta W/\gamma\mathcal{P} \tag{21}$$

Figure 8 illustrates the principles of this procedure.

Capillary Rise Method

In a similar manner, the equation for capillary rise for a nonzero contact angle can be modified to read

$$\cos \Theta = \frac{\Delta\rho r g h}{2\gamma} \tag{22}$$

Rate of Penetration

Washburn of the National Bureau of Standards (now NIST) has developed an equation from the capillary rise equation which relates the rate of penetration of liquid into a bulk sample of powdered material to the surface tension of the penetrating liquid and the contact angle between the liquid and the powder [*61*]. This equation can be used with known materials to back calculate the contact angle as

$$\cos \Theta = \frac{4\nu\eta l}{\gamma r} \tag{23}$$

where l is the length of the capillary path in the powder, r is the average pore size, ν is the velocity of penetration, and η is the viscosity of the penetrating liquid. This equation can be used to estimate wetting properties and kinetics in the dispersion of pigments. A more recent discussion of this problem is given by Letelier et al. [*62*].

SOME SPECIFIC APPLICATIONS OF SURFACE ENERGETICS TO ORGANIC COATINGS

Coatings Application and Defects

Flow phenomena, and their control, at surfaces are very important to coatings film application technology [*6,63*]. The creation of uniform thin films at high speeds involves many problems that are determined by a combination of the application geometry, the velocity of the substrate relative to the liquid coating, the physical properties of the liquid coating, especially the energetics of the surface of the liquid coating, the surface of the substrate, and the new liquid/solid and gas/

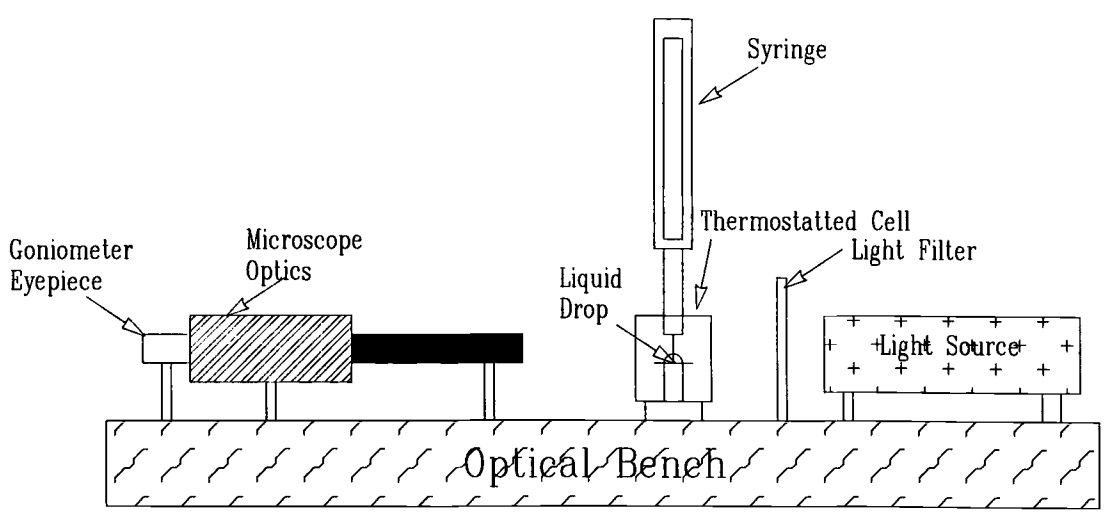

FIG. 14–Schematic of contact angle goniometer.

liquid interfaces created in the application processes. Analysis of several application techniques is given below to illustrate the importance of the use of concepts discussed in the prior portion of this chapter.

Dip Coating

Dip coating is a coating method in which a sheet of material is constantly withdrawn vertically from a coating liquid bath at constant velocity, producing a constant film thickness coating adhering to the sheet, which is usually then dried or cured to produce the final coating on the sheet (see Fig. 15). This problem was originally analyzed by Landau and Levich [*64*], and its solution has been given in modern form by Probstein [*65*]. Only the solution of the problem will be given here, but it is representative of the problems identified by chemical engineers as coating flows. In these cases, the geometry of the coating device, the relative velocity, v, of the object to be coated, and the physical properties of the coating fluid (surface tension, γ; viscosity, η; density, ρ; and acceleration of gravity, g) fix the solution to the coating flow problem. In this case, the limiting film thickness, δ_f, at large distances from the coating bath surface, is given by

$$\delta_f = 0.946 \frac{(\eta v)^{2/3}}{\gamma^{1/6}\sqrt{\rho g}} \tag{24}$$

This solution is derived from the physical effects of surface tension, as described above, plus the Navier-Stokes equation fluid mechanics. These authors assume Newtonian viscosity behavior of the liquid, i.e., the viscosity, η, is independent of shear rate, time-independent surface tension, and an absence of surface tension gradient-driven flows (Marangoi flows), with the appropriate boundary conditions determined by the coating process. This solution can be used by the coating designer and user to establish a first order estimate of the film thickness of the liquid film by the properties of the coating and the velocity of sheet withdrawal.

Curtain Coating

As described above in the section on measurement of dynamic surface tension, analysis of the curtain coating process has yielded a measurement method for dynamic surface tension. In the analyses of this problem, Brown [*45*] and Havenburgh and Joos [*46*] both modeled curtain coating by a falling liquid film held in place by two vertical wires (see Fig. 16). The flux Q of falling liquid is

$$Q = v_0 h_0 \tag{25}$$

where v_0 is the velocity of the falling film and h_0 is the width of the falling film at time zero at the slot through which the liquid exits. The velocity of the falling film at a position x from the slot is given by

$$v^2 = v_0^2 + 2gx \tag{26}$$

where g is the acceleration of gravity. Since the flux of material is constant through the slot, we know that

$$Q = v_0 h_0 = hv \tag{27}$$

and therefore

$$h(x) = \frac{Q}{\sqrt{v_0^2 + 2gx}} \tag{28}$$

This equation gives the user a description of the thickness of liquid film as a function of distance from the slot of the curtain coater. This can also be used to estimate the surface tension at a given position x [*46*] by the following relation

$$\gamma(x) = \frac{\rho h(x) v_0^2}{2} \tag{29}$$

These equations give the application engineer a reasonably complete description of the curtain coating process.

Electrostatic Spray

The application of surface energetics to the problem of charged liquid droplets was first done by Rayleigh [*66*]. In this study, the electrical repulsion forces between charges on a drop are equated to the surface tension forces holding a drop together to give the following equation as an estimate of the upper limit on the charge that can be held on a drop

$$q = \sqrt{16\pi\epsilon r^2 \gamma} \tag{30}$$

where ϵ is the dielectric constant of the drop and r is the drop radius. This can be used to gain an estimate of the drop size in electrostatic spray of liquid paints. Further stability analysis

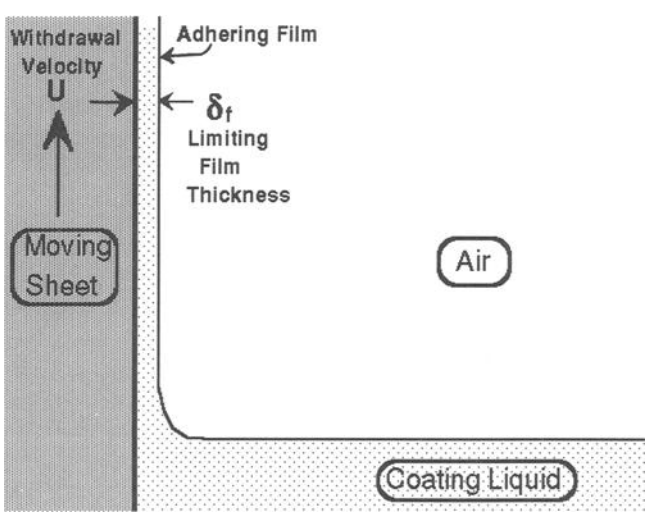

FIG. 15–Schematic of dip coating process.

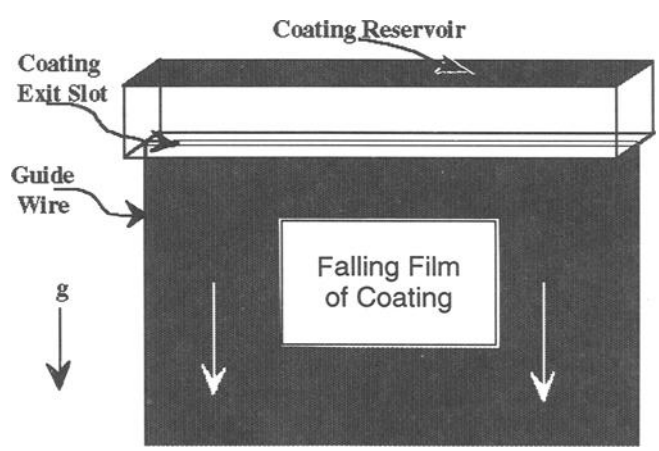

FIG. 16–Schematic of curtain coater.

of this problem indicates that if a drop at this charge limit breaks up, the total energy of the system will be minimized if it does so into n droplets, where n is given by

$$n = \frac{q^2}{4\pi\epsilon r_0^2} \tag{31}$$

where r_0 is the radius of the original drop [67]. This charge limit has been studied and verified experimentally by several workers [68,69] and also applied to problems of spray painting [70]. All of this work further illustrates the importance and extensive applications of surface energetics to coatings use.

Cleaning and Pretreatment of Substrates for Coating

A very important step in the total process of creating a high performance organic coating/substrate system is the cleaning and pretreatment of the substrate prior to the coating application step. The specific purpose of cleaning and pretreating substrate surfaces is to control and/or modify the surface energy of the substrate so that a coating may be successfully applied to the substrate and that the coating will subsequently adhere properly to the substrate and provide the performance desired. Cleaning, as a general rule, involves the removal of substances foreign to the substrate by a surfactant/detergent solution, followed with rinsing by a solvent that leaves the substrate surface clean of contaminants. This may have to be preceded by a mechanical sandblasting, grinding, sanding, scrubbing, etc., to remove thick layers of mil scale, rust, scum, and other built-up material on what is the real substrate. Vapor or organic solvent degreasing/cleaning is also often used to yield a clean surface for coating. These mechanical cleaning steps, along with the cleaning and rinsing of the surface with low surface tension solutions that leave no residue, are best done just before the coating step lest the surface become recontaminated while stored waiting for the coating step. The goal of all these cleaning procedures is to insure a uniform surface that has a uniform contact angle, usually and desirably zero, for wetting by the coating, and to insure the interface created is the coating liquid/substrate interface only. The mechanical sanding, polishing, etc., will also contribute to a lower contact angle by the surface roughness effect discussed above. Oil, dirt, rust, or other contaminants will give poor and incomplete wetting and poor adhesion of the coating at the contaminated sites. Complete wetting is further assisted by insuring the surface tension of the coating liquid is low so that all air is displaced by the coating and the contact angle between the liquid coating and the substrate is zero, or near to it. The surface tension of the liquid coating is best lowered by the polymer of the system or by surfactant additives to the liquid system. Attempts to control the surface tension by the solvent can cause problems in having the surface tension increase as the solvent evaporates.

Substrate pretreatment is usually performed just after the cleaning discussed above and is done to further insure complete wetting and adhesion of the coating, as well as, in the case of metallic substrates, to deposit a corrosion inhibitive layer. In the case of plastic substrates, the pretreatment may be corona or flame modification to oxidize the surface layer and lower the contact angle to near zero. Metal pretreatments often involve the deposition or creation of a rough-surfaced crystalline layer of metallic phosphates which give an easily wetted surface.

SUMMARY

The concepts of surface energy, surface tension, and wetting and contact angle phenomena are of exceptional importance to the science and technology of organic coating. Their understanding is vital for the proper formulation and application of coating. Many of the features of the final organic coating/substrate system are controlled by proper understanding of the surfaces of the liquid coating and the substrate, as well as creation of a proper coating/substrate interface. Both the static and dynamic aspects of liquid surface properties should be considered and the dynamic aspects properly accounted for in coating production and application. These concepts have been reviewed, and references to further reading in this important area of organic coatings science have been given.

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Solubility Parameters

by Charles M. Hansen[1]

NOMENCLATURE

- C Dispersion cohesion energy from Fig. 2 and Fig. 3
- D Dispersion cohesion (solubility) parameter—in tables and computer printouts
- DM Dipole moment—Debyes
- ΔE_d Dispersion cohesion energy
- ΔE_p Polar cohesion energy
- ΔE_h Hydrogen bonding cohesion energy
- ΔE_v Energy of vaporization (=) cohesion energy
- ΔG^M Molar free energy of mixing
- H Hydrogen bonding cohesion (solubility) parameter—in tables and computer printouts
- ΔH_v Molar heat of vaporization
- ΔH^M Molar heat of mixing
- P Polar cohesion (solubility) parameter—in tables and computer printouts
- R Gas constant (1.987 cal/mole-°K)
- R_s Distance in Hansen space
- R_0 Radius of interaction sphere in Hansen space
- RED Relative energy difference, R_s/R_0
- ΔS^M Molar entropy of mixing
- T Absolute temperature
- T_b (Normal) boiling point
- T_c Critical temperature
- V_M Molar volume
- Δ_T Lydersen critical temperature group contribution
- α Thermal expansion coefficient
- δ_d Dispersion cohesion (solubility) parameter
- δ_h Hydrogen bonding cohesion (solubility) parameter
- δ_p Polar cohesion (solubility) parameter
- δ_T Total cohesion (solubility) parameter
- ϕ_i Volume fraction of component "i"
- χ Polymer-liquid interaction parameter (Flory-Huggins)

INTRODUCTION

SOLUBILITY PARAMETERS ARE USED in the coatings industry to select solvents. Liquids with similar solubility parameters will be miscible, and polymers will dissolve in solvents whose solubility parameters are not too different from their own. The basic principle is "like dissolves like." Solubility parameters help put numbers into this simple qualitative idea.

The solubility parameter approach has been used for many years to select solvents for coating materials. The lack of total success has stimulated research. The skill with which solvents can be optimally selected with respect to cost, solvency, workplace environment, external environment, evaporation rate, flash point, etc. has improved over the years as a result of a series of improvements in the solubility parameter concept and widespread use of computer techniques. Most, if not all, commercial suppliers of solvents have computer programs to help with solvent selection. One can now easily predict how to dissolve a given polymer in a mixture of two solvents, neither of which can dissolve the polymer by itself.

This contribution to the paint testing manual unfortunately can not include discussion of all of the significant efforts leading to our present state of knowledge of the solubility parameter. An attempt is made to outline developments, provide some background for a basic understanding, and give examples of uses in practice. The key is to determine which affinities the important components in a system have for each other. For coatings, this means affinities of solvents, polymers, pigment surfaces, additives, and substrates.

It is noteworthy that the concepts presented here have developed toward not just predicting solubility, which requires high affinity between solvent and solute, but to predict affinities between different polymers leading to compatibility, and affinities to surfaces to improve pigment dispersion and adhesion. Attempts are also being made to extend these developments, largely attributable to the coatings industry, to understand affinities and phenomena for a large number of other materials not specifically related to coatings. In these applications the solubility parameter has become a tool, using well-defined liquids as energy probes, to measure the similarity, or lack of same, of key components. Materials with widely different chemical structures may be very close in affinities. Only those materials which interact differently with different solvents can be characterized in this manner. Many inorganic materials, such as fillers, do not interact differently with these energy probes since their energies are very much higher. Changing their surface energies by various treatments can lead to a surface which can be characterized.

Solubility parameters are cohesion energy parameters since they derive from the energy required to convert a liquid to a gas. The energy of vaporization is a direct measure of the total (cohesive) energy holding the liquid's molecules together. All types of bonds holding the liquid together are broken by evaporation, which has led to the concepts described in more detail below. The term cohesion energy pa-

[1]FORCE Institute, Division for Mechatronic and Sensor Technology, Park Alle 345, DK-2605 Broendby, Denmark.

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rameter is more appropriately used when referring to surface phenomena.

HILDEBRAND PARAMETERS

The term solubility parameter was first used by Hildebrand and Scott [*1,2*]. The solubility parameter is the square root of the cohesive energy density

$$\delta = (c \cdot e \cdot d)^{1/2} = \left(\frac{\Delta E_v}{V_M}\right)^{1/2} (\text{cal/cm}^3)^{1/2} \text{ or MPa}^{1/2} \quad (1)$$

where V_M is the molar volume and ΔE_v is the (measurable) energy of vaporization (see Eq 12). The solubility parameter is an important quantity in predicting solubility relations, as can be seen from the following brief introduction.

Thermodynamics requires that the free energy of mixing must be zero or negative for the solution process to occur spontaneously. The free energy change for the solution process is given by the relation

$$\Delta G^M = \Delta H^M - T\Delta S^M \quad (2)$$

where ΔG^M is the free energy of mixing, ΔH^M is the heat of mixing, T is the absolute temperature, and ΔS^M is the entropy change in the mixing process.

The heat of mixing, ΔH^M, is given by Hildebrand and Scott as

$$\Delta H^M \approx \Delta E^M = \phi_1 \phi_2 V_M (\delta_1 - \delta_2)^2 \quad (3)$$

where the ϕ's are volume fractions and V_M is the average molar volume of the solvent. It is important to note that the solubility parameter, or rather the difference in solubility parameters for the solvent-solute combination, is important in determining the solubility. It is clear that a match in solubility parameters leads to a zero heat of mixing, and the entropy change should ensure solution. The maximum difference in solubility parameters which can be tolerated where solution still occurs is found by setting the free energy change equal to zero in Eq 2. It is, in fact, the entropy change which dictates how closely the solubility parameters must match each other. It can also be seen that solvents with smaller molecular volumes promote lower heats of mixing, which, in turn, means that smaller solvent molecules will be thermodynamically better than larger ones when their solubility parameters are equal. A practical aspect of this effect is that solvents with relatively low molecular volumes, such as methanol and acetone, can dissolve a polymer at larger solubility parameter differences than expected from comparisons with other solvents with larger molecular volumes. The converse is also true. Larger molecular species may not dissolve, even though solubility parameter considerations might predict this. This can be a difficulty with plasticizers.

A serious shortcoming of the Hildebrand approach is that negative heats of mixing are not possible. Likewise, the approach is limited to regular solutions as defined by Hildebrand and Scott [*2*] and does not account for association between molecules, such as polar and hydrogen bonding interactions would require. The latter problem seems to have been largely solved with the use of multicomponent solubility parameters. The price has been that no thermodynamic calculations of the heat of mixing in the traditional sense seem possible. This is both because of a lack of detailed theory for this purpose and because of the lack of accuracy with which the solubility parameters can be assigned.

A more detailed description of the theory presented by Hildebrand and the succession of research reports which have attempted to improve on it can be found in Barton's extensive handbook [*3*]. The slightly older excellent contribution of Gardon and Teas [*4*] is also a good source, particularly for coatings and adhesion phenomena. The approach of Burrell [*5*], who divided solvents into hydrogen bonding classes, has found numerous practical applications, and the approach of Blanks and Prausnitz [*6*], who divided the solubility parameter into two components, nonpolar and "polar," are worthy of mention, however, in that these have found wide use and greatly influenced the author's earlier activities, respectively.

It can be seen from Eq 2 that the entropy change can be considered beneficial to mixing. When multiplied by the temperature this will work in the direction of promoting a more negative free energy of mixing. Higher temperatures will also promote this more negative free energy change. The entropy changes associated with polymer solutions will be smaller than those associated with liquid-liquid miscibility, for example, since the "monomers" are already bound into the configuration dictated by the polymer they make up. They are no longer free in the sense of a liquid solvent and can not mix freely to contribute to a larger entropy change. This is one reason polymer-polymer miscibility is difficult to achieve. The free energy criterion dictates that the polymer solubility parameters match extremely well since there is little help from the entropy contribution when progressively larger molecules are involved. However, polymer-polymer miscibility can be promoted by introduction of suitable copolymers or comonomers which interact specifically within the system.

HANSEN SOLUBILITY PARAMETERS

A widely used solubility parameter approach to predicting polymer solubility is that proposed by the author. The basis of these so-called Hansen solubility parameters is that the total energy of vaporization of a liquid consists of several individual parts [*7–11*]. Needless to say, without the work of Hildebrand and Scott [*1,2*] and others not specifically referenced here such as Scatchard, this postulate could never have been made. The total cohesive energy, ΔE_t, can be measured by evaporating the liquid, i.e., breaking all the cohesive bonds. It should also be noted that these cohesive energies arise from interactions of a given solvent molecule with another of its own kind. The basis of the approach is, therefore, very simple, and it is surprising that so many different applications have been possible over the past 25 years. A number of applications are discussed below. A lucid discussion by Barton [*12*] enumerates typical situations where problems occur when using solubility parameters. These are most often where the environment causes the solvent molecules to interact with or within themselves differently than when they make up their own environment, i.e., as pure liquids.

Materials having similar (Hansen) solubility parameters have high affinity for each other. The extent of the similarity in a given situation determines the extent of the interaction. The same can not be said of the total or Hildebrand solubility parameter [*1,2*]. Ethanol and nitromethane, for example,

have similar total solubility parameters (26.1 versus 25.1 $MPa^{1/2}$, respectively), but their affinities are quite different. Ethanol is water soluble, while nitromethane is not. Indeed, mixtures of nitroparaffins and alcohols were demonstrated in many cases to provide synergistic mixtures of two nonsolvents which dissolved polymers [7].

There are three major types of interaction in common organic materials. The most general are the "nonpolar" interactions, which derive from atomic forces. These have also been called dispersion interactions in the literature. Since molecules are built up from atoms, all molecules will contain this type of attractive force. For the saturated aliphatic hydrocarbons, for example, these are essentially the only cohesive interactions, and the energy of vaporization is assumed to be the same as the dispersion cohesive energy, ΔE_d. Finding the dispersion cohesive energy as the cohesion energy of the homomorph, or hydrocarbon counterpart, is the starting point for the calculation of the three Hansen parameters for a given liquid.

The permanent dipole–permanent dipole interactions cause a second type of cohesion energy, the polar cohesive energy, ΔE_p. These are inherently molecular interactions and are found in most molecules to one extent or another. The dipole moment is the primary parameter in calculating these interactions. A molecule can be primarily polar in character without being water soluble, so there is misuse of the term "polar" in the general literature. The polar solubility parameters referred to here are well-defined, experimentally verified, and can be estimated from molecular parameters as described below. As noted above, the polar solvents include those with relatively high total solubility parameters which are not particularly water soluble such as nitroparaffins, propylene carbonate, tri-n-butyl phosphate, and the like. Induced dipoles have not specifically been treated by Hansen, but are recognized as a potentially important factor, particularly for solvents with zero dipole moments.

The third major cohesive energy source is hydrogen bonding, ΔE_h. Hydrogen bonding is a molecular interaction and resembles the polar interactions in this respect. The basis of this type of cohesive energy is attraction among molecules because of the hydrogen bonds. In this perhaps oversimplified approach, the hydrogen bonding parameter has been used to more or less collect the energies from interactions not included in the other two parameters. Alcohols, glycols, carboxylic acids, and other hydrophilic materials have high hydrogen bonding parameters. Other researchers have divided this parameter into separate parts, for example, acid and base cohesion parameters, to allow both positive and negative heats of mixing. These approaches will not be dealt with here, but can be found described in Barton's Handbook [3], and elsewhere [13–15]. The most extensive division of the cohesive energy has been done by Karger et al. [16], who developed a system with five parameters: dispersion, orientation, induction, proton donor, and proton acceptor. The Hansen hydrogen-bonding parameter may be termed an electron interchange parameter as well. As a single parameter it has remarkably well accounted for the experience of the author and keeps the number of parameters to a level which allows ready practical usage.

It is clear that there are other sources of cohesion energy in various types of molecules arising, for example, from induced dipoles, metallic bonds, electrostatic interactions, or whatever type of separate energy can be defined. Hansen stopped with the three major types found in organic molecules. It was and is recognized that additional parameters could be assigned to separate energy types. The description of organometallic compounds could be an intriguing study, for example. This would presumably parallel similar characterizations of surface-active materials, where each separate part of the molecule requires separate characterization for completeness. The Hansen parameters have mainly been used in connection with solubility relations, mostly, but not exclusively, in the coatings industry.

Solubility and swelling have been used to confirm the solubility parameter assignments of many of the liquids. These have then been used to derive group contribution methods and suitable equations based on molecular properties to arrive at estimates of the three parameters for additional liquids. The goal of a prediction is to determine similarity or not of the cohesion energy density parameters. The strength of a particular type of hydrogen bond or other bond, for example, is important only to the extent that it influences the cohesive energy density.

Hansen parameters do have direct application in other scientific disciplines of interest to the coatings industry, such as surface science, where they have been used to characterize the wettability of various surfaces and adsorption properties of pigment surfaces [4,8,10,17–19]. Many other applications of widely different character have been discussed by Barton [3] and Gardon [20]. Surface characterizations have not been given the attention deserved in terms of a unified similarity-of-energy approach. The author can certify that thinking in terms of similarity of energy, whether surface energy or cohesive energy, can lead to rapid decisions and plans of action in critical situations where data are lacking. In other words, the everyday industrial crisis situation can often be reduced in scope by appropriate systematic approaches based on similarity of energy.

The basic equation which governs the assignment of Hansen parameters is that the total cohesion energy, ΔE_t, must be the sum of the individual energies which make it up

$$\Delta E_t = \Delta E_d + \Delta E_p + \Delta E_h \tag{4}$$

Dividing this by the molar volume gives the square of the total (or Hildebrand) solubility parameter as sum of the squares of the Hansen D, P, and H components.

$$\frac{\Delta E_t}{V_M} = \frac{\Delta E_d}{V_M} + \frac{\Delta E_p}{V_M} + \frac{\Delta E_h}{V_M} \tag{5}$$

$$\begin{aligned} \delta_t &= \delta_d^2 + \delta_p^2 + \delta_h^2 \\ &= D^2 + P^2 + H^2 \text{ (computer printouts)} \end{aligned} \tag{6}$$

METHODS AND PROBLEMS IN THE DETERMINATION OF PARTIAL SOLUBILITY PARAMETERS

The best method to calculate Hansen solubility parameters depends to a great extent on what data are available. Hansen originally adopted an essentially experimental procedure and established numbers for 90 liquids based on solubility data for 32 polymers [7]. This procedure involved calculation of the nonpolar parameter according to the procedure outlined

by Blanks and Prausnitz [*6*]. This calculational procedure is still in use and is considered the most reliable and consistent for this parameter. It is outlined below. The division of the remaining cohesive energy between the polar and hydrogen bonding interactions was done by trial and error to fit experimental polymer solubility data. A key to parameter assignments in this initial trial and error approach was that mixtures of two nonsolvents could be systematically found to synergistically (but predictably) dissolve given polymers. This meant that these had parameters placing them on opposite sides of the solubility region, a spheroid, from each other. Having a large number of such predictably synergistic systems as a basis, reasonably accurate divisions into the three energy types were possible.

Using the experimentally established, approximate, δ_p and δ_h parameters, Skaarup [*9*] found that the Böttcher equation could be used to calculate the polar parameter quite well, and this led to a revision of the earlier values to those now in wide use for these same liquids. These values were also consistent with the eperimental solubility data for 32 polymers available at that time and Eq 6. Furthermore, Skaarup developed the equation for the solubility parameter "distance," R_s, between two materials based on their respective partial solubility parameter components

$$R_s = 4(\delta_{d_1} - \delta_{d_2})^2 + (\delta_{p_1} - \delta_{p_2})^2 + (\delta_{h_1} - \delta_{h_2})^2 \qquad (7)$$

This equation was developed from plots of experimental data where the constant 4 was found convenient and correctly represented the solubility data as a sphere encompassing the good solvents. When the scale for the dispersion parameter is doubled compared with the other two parameters, essentially spherical rather than spheroidal, regions of solubility are found. This greatly aids two-dimensional plotting and visualization. There are, of course, boundary regions where deviations can occur. These are most frequently found to involve the larger molecular species being less effective solvents compared with the smaller counterparts which define the solubility sphere. Likewise smaller molecular species, such as acetone and methanol, often appear as outliers in that they dissolve a polymer even though they have solubility parameters placing them at a distance greater than the solubility sphere radius, R_0. This dependence on molar volume is inherent in the theory developed by Hildebrand and Scatchard as discussed above. Smaller molar volume favors lower heats of mixing, which in turn promotes solubility. Such smaller molecular volume species which dissolve "better" than predicted by comparisons based on solubility parameters alone should not necessarily be considered outliers. This statement is justified by Eq 3, where it can be seen that the molar volume and the square of the solubility parameter difference are weighted equally in estimating the heat of mixing in the Hildebrand theory.

The molar volume is frequently used as a fourth parameter to describe molecular size effects. These are especially important in correlating diffusional phenomena with the solubility parameter, for example. The author has preferred to retain the three, well-defined, partial solubility parameters with a separate, fourth, molar volume parameter, rather than to multiply the solubility parameters by the molar volume raised to some power to redefine them.

The exact reason for the constant 4 in Eq 7 is not clear, but it is currently considered more as an experimental result related to the entropy changes in the systems described rather than a theoretically well-defined constant. The author has also found in unpublished studies that values close to 5 represented solubility data equally well for the cases studied. It is thought that this constant especially reflects the entropy change beneficial to the solution process when the molecular interactions characterized by the δ_p and δ_h parameters are involved. The order in the pure liquids is reduced when they dissolve a polymer of lower solubility parameter (degree of order). This entropy change favors the dissolution process. Thus more polar and hydrogen bonded liquids can dissolve polymers of lower polar and hydrogen bonding character. The differences in solubility parameters between the solvent and solute in the polar and hydrogen bonding parameters are larger by a factor of two than is tolerated when nonpolar solvents dissolve the same polymer. This factor of 2 is squared to give the "4" in Eq 7.

Another way to view this is as follows. It is assumed that the (center-of-the-sphere) partial solubility parameters assigned by computer optimization techniques to polymers using Eq 7 are the theoretically correct ones. A solvent with parameters corresponding to the center is to be changed in quality. If the nonpolar parameter difference only is changed by one unit, the effect on R_s is four units. If the polar or hydrogen bonding parameter difference is changed by one unit, the effect on R_s is also one unit. The entropy changes associated with the polar and hydrogen interactions have reduced the total (free energy change) effect by a factor of 4 and are thus four times larger than those associated with the nonpolar interactions.

What is more probable is that the entropy changes on solution from the polar and hydrogen bonding interactions are some function of the solubility parameters and, in fact, increase with increasing polar or hydrogen bonding parameter difference between solvent and solute. If this is, indeed, true, then the currently assigned polar and hydrogen bonding parameters for the polymers are too high. Exactly what they should be from a theoretical point of view remains to be elucidated by future research. This is one reason the calculation of partial polymer solubility parameters by group contributions has not provided good agreement with the computer optimizations of experimental data.

The discussion above follows from the fact that the boundaries of the regions of solubility are characterized by a free energy change of zero for the solution process. The Flory-Huggins limiting chi parameter, χ, of about 0.5 is also characteristic for the boundary of the solubility region. Patterson [*21*], in particular, has been instrumental in showing the relations between the chi parameter and solubility parameters. A polymer of molecular weight approaching infinity will have a chi parameter of 0.5 and just be soluble [*4,6,22*]. This is strictly valid only for the interactions described by this theory. So-called theta solvents will also be located in boundary regions on solubility parameter plots with these same restrictions. Much polymer research has focused on these boundary regions only, for the above reasons and because relatively small changes in temperature, molecular weight, solvent quality, etc. give large easily measureable changes in other quantities.

The approach of computer optimizing solubility data to spheres which is currently in use still seems most favorable, at least until an improvement is offered by an improved theory. Plotting experimental solubility data defines boundaries of solubility, which in fact are fixed by the free energy of mixing being experimentally equal to zero. It should be recognized that using solubility parameters, which relate to the heat of mixing only, emphasizes the practical/empirical nature of this practical approach and reinforces the use of the term cohesion parameters.

Equation 7 is readily used on a computer (or on a hand calculator), and supplementary relations allow easier scanning of large sets of data. It is obvious that solubility, or high affinity, requires that R_s be less than R_0. The ratio R_s/R_0 has been called the RED number, reflecting the Relative Energy Difference. A RED number of 0 is found for no energy difference. RED numbers less than 1.0 indicate high affinity, RED equal to or close to 1.0 is a boundary condition, and progressively higher RED numbers indicate progressively lower affinities. Scanning a sizeable (the author has Hansen solubility parameters for about 850 liquids) computer output for RED numbers less than 1.0, for example, rapidly allows location of the most interesting liquids for a given application.

The revised set of parameters for the 90 solvents was the basis for group contribution procedures developed by (most notably) Van Krevelen [*23*] and Beerbower [*11,24*], who also used Fedors work [*25*]. These various developments have been summarized by Barton [*3*], although Beerbower's latest values have only appeared in the NASA document [*24*]. Table 1 is an expanded table of Beerbower group contributions which was distributed among those who were in contact with Beerbower in the late 1970s. Beerbower also developed a simple equation for the polar parameter [*11*], which involved only the dipole moment and the square root of the molar volume. This is also given below and has been found quite reliable by Koehnen and Smolders [*26*]. This equation has also been found reliable by the author as well, giving results generally consistent with Eq 6, which, again, is the basis of the whole approach. Koehnen and Smolders also give correlation coefficients for other calculational procedures to arrive at the individual Hansen parameters.

A sizeable number of liquids have now been assigned Hansen parameters using the procedures described here. Many of these have not been published. Exxon Chemical Corporation [*27,28*] has indicated a computer program with data for over 500 solvents and plasticizers, 450 resins and polymers, and 500 pesticides. The author's files contain the three parameters for about 850 liquids, although several of them appear with two or three sets of possible values awaiting experimental confirmation. In some cases this is due to questionable physical data, for example, for latent heats of vaporization or wide variations in reported dipole moments. Another reason for this is that some liquids are chameleonic [*29*] as defined by Hoy in that they adopt configurations depending on their environment. Hoy [*29*] cites the formation of cyclic structures for glycol ethers with (nominally) linear structure. The formation of hydrogen bonded tetramers of alcohols in a fluoropolymer has also been cited [*30*]. The term "compound formation" can be found in the older literature, particularly where mixtures with water were involved, and structured species were postulated to explain phenomena based on specific interactions among the components of the mixtures. Barton has recently discussed some of these situations and points out that Hildebrand or Hansen parameters must be used with particular caution where the extent of donor-acceptor interactions, and in particular hydrogen bonding within a compound, is very different from that between compounds [*12*]. Amines, for example, are known to associate with each other. Pure component data can not be expected to predict the behavior in such cases.

Still another reason for difficulties is the large variation of dipole moments reported for the same liquid. The dipole moment for some liquids depends on their environment, as discussed below. A given solvent can be listed with different values in files to keep these phenomena in mind.

Large data sources greatly enhance searching for similar materials and locating new solvents for a polymer based on limited data, for example. Unfortunately, different authors have used different group contribution techniques, and there is a proliferation of different "Hansen" parameters for the same chemicals in the literature. This would seem to be an unfortunate situation, but may ultimately provide benefits. In particular, partial solubility parameter values found in Hoy's extensive tables [*3,31*] are not compatible with the customary Hansen parameters reported here. Hoy has provided an excellent source of total solubility parameters. He independently arrived at the same type division of cohesion energies as Hansen, although the methods of calculation are quite different.

Many solvent suppliers have also presented tables of solvent properties and/or use computer techniques using these in their technical service. Partial solubility parameters not taken directly from earlier well-documented sources should be used with caution. In particular it can be noted that the Hoy dispersion parameter is consistently lower than that found by Hansen. Hoy subtracts estimated values of the polar and hydrogen bonding energies from the total energy to find the dispersion energy. This allows for more calculational error and underestimates the dispersion energy since the Hoy procedure does not appear to fully separate the polar and hydrogen bonding energies. The Van Krevelen dispersion parameters appear too low. The author has not attempted these calculations, being completely dedicated to the full procedure described here, but values estimated independently based on the Van Krevelen dispersion parameters are clearly low. A comparison with related compounds, or similarity principle, gives better results than those found from the Van Krevelen dispersion group contributions.

In the following, calculational procedures and experience are presented according to the procedures found most reliable for the experimental and/or physical data available for a given liquid.

CALCULATION OF THE DISPERSION SOLUBILITY PARAMETER, δ_d

The δ_d parameter is calculated according to the procedures outlined by Blanks and Prausnitz [*6*]. Figures 1, 2, or 3 can be used to find this parameter depending on whether the molecule of interest is aliphatic, cycloaliphatic, or aromatic. These figures have been inspired by Barton [*3*], who converted

TABLE 1—Group contributions to partial solubility parameters.

Functional Group	Molar Volume,[f] ΔV (cm^3/mol)		London Parameter, $\Delta V\delta_D^2$ (cal/mol)			Polar Parameter, $\Delta V\delta_P^2$ (cal/mol)			Electron Transfer Parameter, $\Delta V\delta_H^2$ (cal/mol)		Total Parameter $\Delta V\delta^2$ (cal/mol)	
	Aliphatic	Aromatic[e]	Alkane	Cyclo	Aromatic	Alkane	Cyclo	Aromatic	Aliphatic	Aromatic	Aliphatic	Aromatic
CH_3^-	33.5	Same	1125	Same	Same	0	0	0	0	0	1 125	Same
$CH_2<$	16.1	Same	1180	Same	Same	0	0	0	0	0	1 180	Same
—CH<	−1.0	Same	820	Same	Same	0	0	0	0	0	820	Same
>C<	−19.2	Same	350	Same	Same	0	0	0	0	0	350	Same
CH_2 = olefin	28.5	Same	850 ± 100	?	?	25 ± 10	?	?	180 ± 75	?	1 030	Same
—CH = olefin	13.5	Same	875 ± 100	?	?	18 ± 5	?	?	180 ± 75	?	1 030	Same
>C = olefin	−5.5	Same	800 ± 100	?	?	60 ± 10	?	?	180 ± 75	?	1 030	Same
Phenyl-	...	71.4	...	...	7530	...	...	50 ± 25	...	50 ± 50[a]	...	7630
C-5 ring (saturated)	16	...	...	250	...	0	0	...	0	...	250	...
C-6 ring	16	Same	...	250	250	0	0	0	0	0	250	250
—F	18.0	22.0	0	0	0	1000 ± 150	?	700 ± 100	0	0	1 000	800[e]
=F_2 twin[d]	40.0	48.0	0	0	0	700 ± 250[a]	?	500 ± 250[a]	0	0	1 700	1360[e]
≡F_3 triplet[d]	66.0	78.0	0	0	0	?	?	?	0	0	1 650	1315[e]
—Cl	24.0	28.0	1400 ± 100	?	1300 ± 100	1250 ± 100	1450 ± 100	800 ± 100	100 ± 20[a]	Same	2 760	2200[e]
=Cl_2 twin[d]	52.0	60.0	3650 ± 160	?	3100 ± 175[a]	800 ± 150	?	400 ± 150[a]	165 ± 10[a]	180 ± 10[a]	4 600	3670[e]
≡Cl_3 triplet[d]	81.9	73.9	4750 ± 300[a]	?	?	300 ± 100	?	?	350 ± 250[a]	?	5 400	4300[e]
—Br	30.0	34.0	1950 ± 300[a]	1500 ± 175	1650 ± 140	1250 ± 100	1700 ± 150	800 ± 100	500 ± 100	500 ± 100	3 700	2960[e]
=Br_2 twin[d]	62.0	70.0	4300 ± 300[a]	?	3500 ± 300[a]	800 ± 250[a]	?	400 ± 150[a]	825 ± 200[a]	800 ± 250[a]	5 900	4700[e]
≡Br_3 triplet[d]	97.2	109.2	5800 ± 400[a]	?	?	350 ± 150[a]	?	?	1500 ± 300[a]	?	7 650	6100[e]
—I	31.5	35.5	2350 ± 250[a]	2200 ± 250[a]	2000 ± 250[a]	1250 ± 100	1350 ± 100	575 ± 100	1000 ± 200[a]	1000 ± 200[a]	4 550	3600[e]
=I_2 twin[d]	66.6	74.6	5500 ± 300[a]	?	4200 ± 300[a]	800 ± 250[a]	?	400 ± 150[a]	1650 ± 250[a]	1800 ± 250[a]	8 000	6400[e]
≡I_3 triplet[d]	111.0	123.0	?	?	?	?	?	?	?	?	11 700	9350[e]
—O— ether	3.8	Same	0	0	0	500 ± 150	600 ± 150	450 ± 150	450 ± 25	1200 ± 100	800	(1650 ± 150)
>CO ketone	10.8	Same	...[c]	2350 ± 400	2800 ± 325	(152 000 ± 7%)/V	1000 ± 300	950 ± 300	800 ± 250[b]	400 ± 125[a]	4 150	Same
—CHO	(23.2)	(31.4)	950 ± 300	?	550 ± 275	2100 ± 200	3000 ± 500	2750 ± 200	1000 ± 200	750 ± 150	(4 050)	Same
—COO-ester	18.0	Same	...[c]	?	...[c]	(56 000 ± 12%)/V	?	(338 000 ± 10%)/V	1250 ± 150	475 ± 100[a]	4 300	Same
—COOH	28.5	Same	3350 ± 300	3550 ± 250	3600 ± 400	500 ± 150	300 ± 50	750 ± 350	2750 ± 250	2250 ± 250[a]	6 600	Same
—OH	10.0	Same	1770 ± 450	1370 ± 500	1870 ± 600	700 ± 200	1100 ± 300	800 ± 150	4650 ± 400	4650 ± 500	7 120	Same
=$(OH)_2$ twin or adjacent	26.0	Same	0	?	?	1500 ± 100	?	?	9000 ± 600	9300 ± 600	10 440	Same
—CN	24.0	Same	1600 ± 850[a]	?	0	4000 ± 800[a]	?	3750 ± 300[a]	500 ± 200[b]	400 ± 125[a]	4 150	Same
—NO_2	24.0	32.0	3000 ± 600	?	2550 ± 125	3600 ± 600	?	1750 ± 100	400 ± 50[b]	350 ± 50[a]	7 000	(4400)
—NH_2 amine	19.2	Same	1050 ± 300	1050 ± 450[a]	150 ± 150[a]	600 ± 200	600 ± 350[a]	800 ± 200	1350 ± 200	2250 ± 200[b]	3 000	Same
>NH_2 amine	4.5	Same	1150 ± 225	?	?	100 ± 50	?	?	750 ± 200	?	2 000	Same
—NH_2 amide	(6.7)	Same	?	?	?	?	?	?	2700 ± 550[a]	?	(5 850)	Same
≥PO_4 ester	28.0	Same	...[c]	?	?	(81 000 ± 10%)/V	?	?	3000 ± 500	?	(7 000)	Same

[a]Based on very limited data. Limits shown are roughly 95% confidence; in many cases, values are for information only and not to be used for computation.
[b]Includes unpublished infrared data.
[c]Use formula in $\Delta V\delta_P^2$ column to calculate, with V for total compound.
[d]Twin and triplet values apply to halogens on the same C atom, except that $\Delta V\delta_P^2$ also includes those on adjacent C atoms.
[e]These values apply to halogens attached directly to the ring and also to halogen attached to aliphatic double-bonded C atoms.
[f]From R. F. Fedors [25].

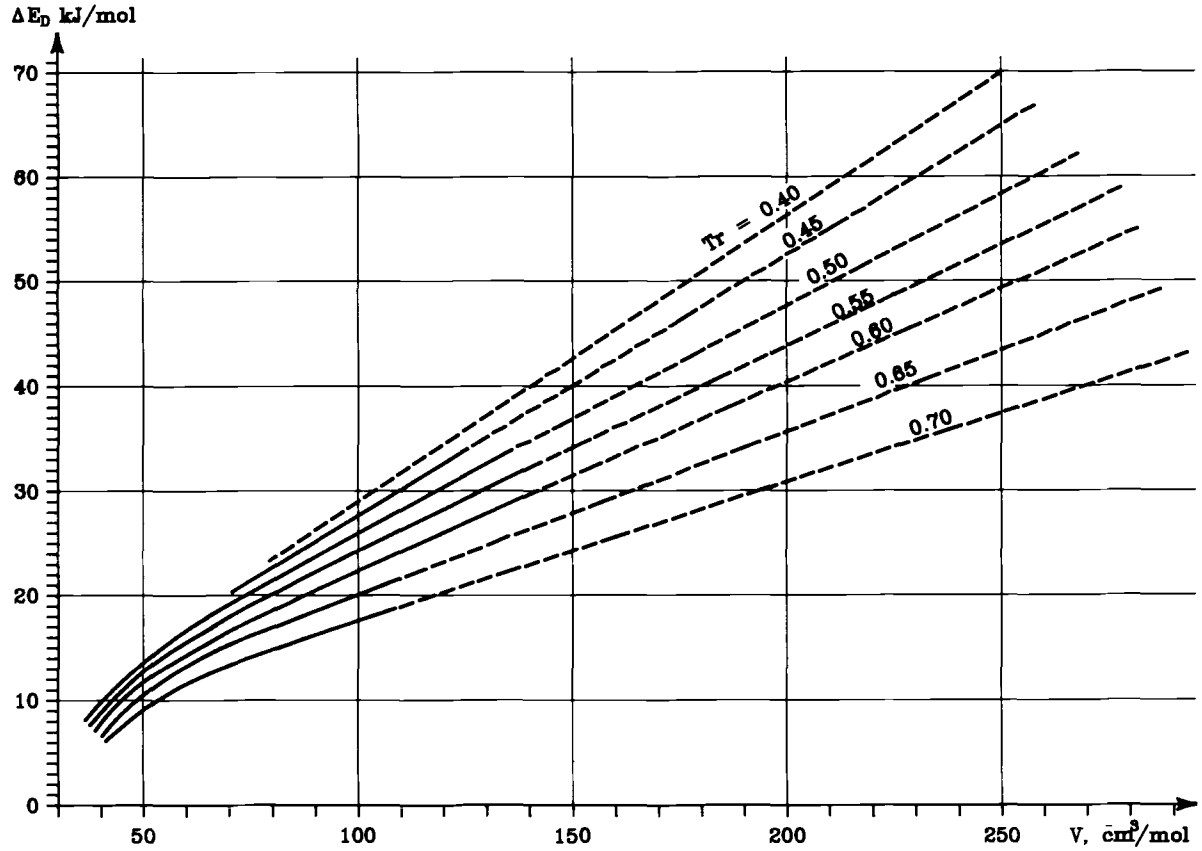

FIG. 1–Energy of vaporization for straight chain hydrocarbons as a function of molar volume and reduced temperature.

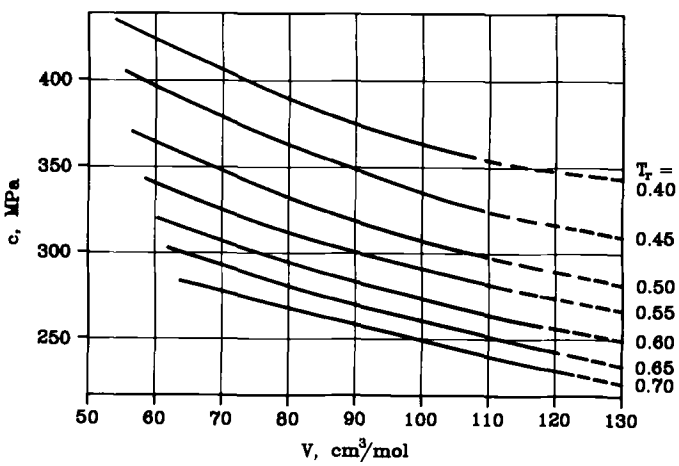

FIG. 2–Cohesive energy density for cycloalkanes as a function of molar volume and reduced temperature.

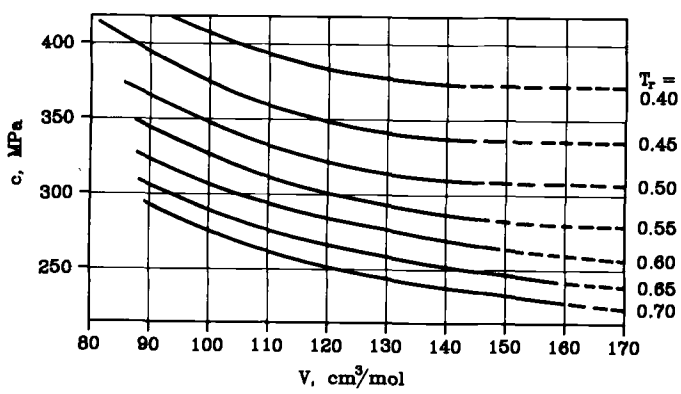

FIG. 3–Cohesive energy density for aromatic hydrocarbons as a function of molar volume and reduced temperature.

earlier data to SI units. All three of these figures have been straight line extrapolated into a higher range of molar volumes than that reported by Barton. Energies found with these extrapolations have also provided consistent results. The solubility parameters in SI units, $MPa^{1/2}$, are 2.0455 times larger than those in the older centimeter, gram, second system, $(cal/cc)^{1/2}$, which still finds extensive use in the United States, for example.

The figure for the aliphatic liquids gives the dispersion cohesive energy, ΔE_d, whereas the other two figures directly report the dispersion cohesive energy density, c. The latter is much simpler to use since one need only take the square root of the value found from the figure to find the respective partial solubility parameter. Barton also presented a similar figure for the aliphatic solvents, but it is inconsistent with the energy figure and in error. Its use is not recommended. When substituted cycloaliphatics or substituted aromatics are considered, simultaneous consideration of the two separate parts of the molecules is required. The dispersion energies are evaluated for each of the types of molecules involved, and a weighted average for the molecule of interest based on numbers of significant atoms is taken. For example, hexyl benzene

would be the arithmetic average of the dispersion energies for an aliphatic and an aromatic liquid, each with the given molar volume of hexyl benzene. Liquids such as chlorobenzene, toluene, and ring compounds with alkyl substitutions with only two or three carbon atoms have been considered as cyclic compounds only. Such weighting has been found necessary to satisfy Eq 6.

The critical temperature, T_c, is required to use the dispersion energy figures. If the critical temperature cannot be found, it must be estimated. A table of the Lydersen group contributions, Δ_T, [32] as given by Hoy [31] for calculation of the critical temperature, is included here as Table 2. In some cases the desired groups may not be in the table, which means some educated guessing is required. The end result does not appear too sensitive to these situations. The normal boiling temperature, T_b, is also required in this calculation. This is not always available, either, and must be estimated by similarity, group contribution, or other technique. The Lydersen group contribution method involves the use of Eqs 8 and 9.

$$T_b/T_c = 0.567 + \Sigma\Delta_T - (\Sigma\Delta_T)^2 \tag{8}$$

and

$$T_r = T/T_c \tag{9}$$

where T has been taken as 298.15 K.

The dispersion parameter is an atomic force parameter. The size of the atom is important. It has been found that corrections are required for atoms significantly larger than carbon, such as chlorine, sulfur, bromine, etc., but not for oxygen or nitrogen, which have a similar size. The carbon atom in hydrocarbons is the basis of the dispersion parameter in its present form. These corrections are applied by first finding the dispersion cohesive energy from the appropriate figure. This requires multiplication by the molar volume for the cyclic compounds using data from the figures here, since these figures give the cohesive energy densities. The dispersion cohesive energy is then increased by adding on the correction factor. This correction factor for chlorine, bromine, and sulfur has been taken as 1650 J/mol for each of these atoms in the molecule. Dividing by the molar volume and then taking the square root gives the (large atom corrected) dispersion solubility parameter.

The need for these corrections has been confirmed many times, both for interpretation of experimental data and to allow Eq 6 to balance. Research is definitely needed in this area. The impact of these corrections is, of course, larger for the smaller molecular species. The taking of square roots of the larger numbers involved with the larger molecular species reduces the errors involved in these cases since the corrections themselves are relatively small.

It can be seen from the dispersion parameters of the cyclic compounds that the ring also has an effect similar to increasing the effective size of the interacting species. The dispersion energies are larger for cycloaliphatic compounds than for their aliphatic counterparts, and they are higher for aromatic compounds than for the corresponding cycloaliphatics. Similar effects also appear with the ester group. This group appears to act as if it were, in effect, an entity which is larger than the corresponding compound containing only carbon (i.e., its homomorph), and it has a higher dispersion solubility parameter without any special need for corrections.

The careful evaluation of the dispersion cohesive energy may not have major impact on the value of the dispersion solubility parameter itself because of the taking of square roots. Larger problems arise because of Eq 4. Energy assigned to the dispersion portion can not be reused when finding the other partial parameters using Eq 4 (or Eq 6). This is one reason group contributions are recommended in some cases below.

CALCULATION OF THE POLAR SOLUBILITY PARAMETER, δ_p

The earliest assignments of a "polar" solubility parameter were given by Blanks and Prausnitz [6]. These parameters were in fact the combined polar and hydrogen bonding parameters as used by Hansen and cannot be considered polar in the current context. The first Hansen polar parameters [7] were reassigned new values by Skaarup according to the Böttcher equation [9]. This equation requires the molar volume, the dipole moment, DM, the refractive index, and the dielectric constant. These are not available for many compounds, and the calculation is somewhat more difficult than using the much simpler equation developed by Beerbower [11]

$$\delta_p = \frac{37.4}{(V_M)^{1/2}}(DM) \tag{10}$$

The constant 37.4 gives this parameter in SI units.

Equation 10 has been consistently used by the author over the past few years, particularly in view of its reported reliability [26]. This reported reliability appears to be correct. The molar volume must be known or estimated in one way or another. This leaves only the dipole moment to be found or estimated. Standard reference works have tables of dipole moments, with the most extensive listing still being McClellan [33]. Other data sources also have this parameter as well as other relevant parameters and data such as latent heats and critical temperatures. The so-called DIPPR database has been found useful for many compounds of reasonably common usage, but many interesting compounds are not included in DIPPR. This abbreviation is for Design Institute for Physical Property Research,[2] Project 801 of the American Institute of Chemical Engineers at the Pennsylvania State University [34]. When no dipole moment is available, similarity with other compounds, group contributions, or experimental data can be used to estimate the polar solubility parameter.

It must be noted that the fact of zero dipole moment in symmetrical molecules is not basis enough to assign a zero polar solubility parameter. An outstanding example of variations of this kind can be found with carbon disulfide. The reported dipole moments are mostly 0 for gas phase measurements, supplemented by 0.08 in hexane, 0.4 in carbon tetrachloride, 0.49 in chlorobenzene, and 1.21 in nitrobenzene.

[2]Design Institute for Physical Property Research, Department of Chemical Engineering, 167 Fenske Laboratory, The Pennsylvania State University, University Park, PA 16802.

TABLE 2—Lydersen group constants.

Group	Aliphatic, ΔT	Cyclic, ΔT	Δ_T^P	Aliphatic, ΔP	Cyclic, ΔP
CH_3	0.020	...	0.0226	0.227	...
CH_2	0.020	0.013	0.0200	0.227	0.184
>CH—	0.012	0.012	0.0131	0.210	0.192
>C<	0.000	−0.007	0.0040	0.210	0.154
$=CH_2$	0.018	...	0.0192	0.198	...
=CH—	0.018	0.011	0.0184	0.198	0.154
=C<	0.000	0.011	0.0129	0.198	0.154
=CH aromatic	...	...	0.0178	...	...
═CH aromatic	...	...	0.0149	...	...
—O—	0.021	0.014	0.0175	0.16	0.12
>O epoxide	...	...	0.0267	...	...
—COO—	0.047	...	0.0497	0.47	...
>C═O	0.040	0.033	0.0400	0.29	0.02
—CHO	0.048	...	0.0445	0.33	...
$—CO_2O$	...	...	0.0863	...	...
—OH→	...	...	0.0343	0.06	...
—H→	...	...	−0.0077	...	...
—OH primary	0.082	...	0.0493	...	...
—OH sec.	...	...	0.0440	...	...
—OH tert.	...	...	0.0593	...	...
—OH phenolic	0.035	...	0.0060	−0.02	
$—NH_2$	0.031	...	0.0345	0.095	...
—NH—	0.031	0.024	0.0274	0.135	0.09
>N—	0.014	0.007	0.0093	0.17	0.13
—C≡N	0.060	...	0.0539	0.36	...
—NCO	...	...	0.0539	...	...
HCON<	...	...	0.0546	...	...
—CONH—	...	...	0.0843	...	...
—CON<	...	...	0.0729	...	...
$—CONH_2$	...	...	0.0897	...	...
—OCONH—	...	...	0.0938	...	...
—S—	0.015	0.008	0.0318	0.27	0.24
—SH	0.015	...	...	...	...
—Cl 1°	0.017	...	0.0311	0.320	...
—Cl 2°	...	...	0.0317	...	...
Cl_2 twin	...	...	0.0521	...	...
Cl aromatic	...	...	0.0245	...	...
—Br	0.010	...	0.0392	0.50	...
—Br aromatic	...	...	0.0313	...	...
—F	0.018	...	0.006	0.224	...
—I	0.012	...	...	0.83	...
Conjugation	...	...	0.0035	...	...
c is double bond	...	...	−0.0010	...	...
trans double bond	...	...	−0.0020	...	...
4 Member ring	...	...	0.0118	...	...
5 Member ring	...	...	0.003	...	...
6 Member ring	...	...	−0.0035	...	...
7 Member ring	...	...	0.0069	...	...
Ortho	...	...	0.0015	...	...
Meta	...	...	0.0010	...	...
Para	...	...	0.0060	...	...
Bicycloheptyl	...	...	0.0034	...	...
Tricyclodecane	...	...	0.0095	...	...

There is a clear increase with increasing solubility parameter of the media. The latter and highest value has been found experimentally most fitting for correlating permeation through a fluoropolymer film used for chemical protective clothing [*35*]. Many fluoropolymers have considerable polarity. The lower dipole moments seem to fit in other instances. Diethylether has also presented problems as an outlier in terms of dissolving or not, or rapid permeation or not. Here the reported dipole moments [*33*] vary from 0.74 to 2.0 with a preferred value of 1.17, and with 1.79 in chloroform. Choosing a given value seems rather arbitrary. The chameleonic cyclic forms of the linear glycol ethers would also seem to provide for a basis of altered dipole moments in various media [*29*].

When Eq 10 can not be used, the polar solubility parameter has been found using the Beerbower table of group contributions, by similarity to related compounds, and/or by subtraction of the dispersion and hydrogen bonding cohesive energies from the total cohesive energy. The question in each case is: "Which data are available and judged most reliable?" New group contributions have also been developed from related compounds where their dipole moments are available. These new polar group contributions then become supplementary to the Beerbower table.

For large molecules, especially those with long hydrocarbon chains, the accurate calculation of the relatively small polar (and hydrogen bonding) contributions present special difficulties. The latent heats are not generally available with sufficient accuracy to allow subtraction of two large numbers from each other to find a very small one. In such cases the similarity and group contribution methods are thought best. Unfortunately, latent heats found in a widely used handbook [*36*] are not clearly reported as to the reference temperature. There is an indication that these are 25°C data, but checking indicated many of the data were identical with boiling point data reported elsewhere in the literature. A more recent edition of this handbook has a completely different and less voluminous section for the latent heat of evaporation [*37*]. Again, even moderate variations in reported heats of vaporization can cause severe problems in calculating the polar (or hydrogen bonding) parameter when Eqs 4 or 6 are strictly adhered to.

CALCULATION OF THE HYDROGEN BONDING SOLUBILITY PARAMETER, δ_h

In the earliest work, the hydrogen bonding parameter was almost always found from the subtraction of the polar and dispersion energies of vaporization from the total energy of vaporization. This is still widely used where the required data are available and reliable. At this stage, however, the group contribution techniques are considered reasonably reliable for most of the required calculations and, in fact, more reliable than estimating several of the other parameters to ultimately arrive at the subtraction step just mentioned. Therefore, in the absence of reliable latent heat and dipole moment data, group contributions are judged to be the best alternative. Similarity to related compounds can also be used, of course, and the result of such a procedure should be essentially the same as for using group contributions.

SUPPLEMENTARY CALCULATIONS AND PROCEDURES

The procedures listed above are those most frequently used by the author in calculating the three partial solubility parameters for liquids where some data are available. There are a number of other calculations and procedures which are also helpful. Latent heat data at 25°C have consistently been found from latent heats at another temperature using the relation given by Fishtine [*38*].

$$\frac{\Delta H_v(T_1)}{\Delta H_v(T_2)} = \left[\frac{T_c - T_1}{T_c - T_2}\right]^{0.38} = \left[\frac{1 - T_{r1}}{1 - T_{r2}}\right]^{0.38} \left[\frac{1 - T_{r1}}{1 - T_{r2}}\right]^{0.38} \tag{11}$$

This is done even if the melting point of the compound being considered is higher than 25°C. The result is consistent with all the other parameters, and to date no problems with particularly faulty predictions have been noted in this respect, i.e., it appears as if the predictions are not significantly in error. When the latent heat is given in cal/mole, the above equation is used to estimate the latent heat at 25°C. RT equal to 592 cal/mole is then subtracted from this according to Eq 12 to find the total cohesion energy, ΔE_v, in cgs units at this temperature:

$$\Delta E_v = \Delta E_t = \Delta H_v - RT \tag{12}$$

Only very limited attempts have been made to calculate solubility parameters at a higher temperature. Solubility parameter correlations of phenomena at higher temperatures have generally been found satisfactory when the established 25°C parameters have been used. Recalculation to higher temperatures is possible, but has not been found necessary. In this direct but approximate approach it is assumed that the parameters all demonstrate the same temperature dependence, which, of course, is not the case. It might be noted in this connection that the hydrogen bonding parameter, in particular, is the most sensitive to temperature. As the temperature is increased, more and more hydrogen bonds are progressively broken, and this parameter will decrease more rapidly than the others.

The gas phase dipole moment is not temperature dependent, although the volume of the fluid does change with temperature, which will change its cohesive energy density. Beerbower has suggested relations to predict the changes of the partial solubility parameters with temperature [*11*]. The coefficient of thermal expansion, α, appears in all of these relations. These are

$$\frac{d(\delta_d)}{dT} = -1.25\,\alpha\delta_d \tag{13}$$

$$\frac{d(\delta_p)}{dT} = -0.5\,\alpha\delta_p \tag{14}$$

$$\frac{d(\delta_h)}{dT} = -\delta_h\,(1.22 \times 10^{-3} + 0.5\,\alpha) \tag{15}$$

A computer program has been developed by the author to assign the three Hansen parameters for solvents based on experimental data alone. This has been used in several cases

where the parameters for the given liquids were desired with a high degree of accuracy. The procedure is to enter solvent quality, good or bad, into the program for a reasonably large number of polymers where the solubility parameters and appropriate radius of interaction for the polymers are known. The program then locates that set of δ_d, δ_p, and δ_h parameters for the solvent which best satisfies the requirements of a location within the spheres of the appropriate polymers where solvent quality is good and outside of the appropriate spheres where it is bad.

An additional aid in estimating the Hansen parameters for many compounds is that these parameters can be found by interpolation or extrapolation, especially for homologous series. The first member may not necessarily be a straight line extrapolation, but comparisons with related compounds should always be made where possible to confirm assignments. Plotting the parameters reported in Table 3 for homologous series among the esters, nitroparaffins, ketones, alcohols, and glycol ethers will aid in finding the parameters for related compounds.

Table 3 contains Hansen solubility parameters for a large number of liquids and plasticizers. These are given in SI units.

SOLUBILITY PARAMETERS FOR POLYMERS

The solubility parameters for numerous polymers and film formers are given in Table 4. Suppliers and trademarks are given in Table 5. These data are based on solubility determinations unless otherwise noted. There are four parameters, the three describing the nonpolar, polar, and hydrogen bonding interactions as for the liquids, and the fourth, R_0, a radius of interaction for the type of interaction described. Most of these are taken from a report [*39*] from the Scandinavian Paint and Printing Ink Research Institute. (This institute unfortunately no longer exists.) Additional values have been contributed according to the notes in the table to indicate the types of data which have been correlated with these techniques. Barton [*40*] has also provided solubility parameters for many polymers in a recent handbook.

Experimental determination of polymer solubility parameters involves trying to dissolve the polymer at a given concentration, usually 10% by weight, in a selection of solvents intended to maximize information regarding all types of interaction. Whenever possible the author uses a set of parameters indicated with an "*" in Table 3. The "yes" or "no" solubility data can be plotted by hand or processed by computer to yield a "spherical" characterization as described above. Teas [*41*] has developed a triangular plotting technique which helps visualization of three parameters on a plane sheet of paper. Examples are found in Ref *3* and Ref *4* as well.

Swelling, weight gain, solvent resistance, and surface attack have also been used as a primary data to characterize polymers.

APPLICATIONS

There are many applications documented in the literature where solubility parameters have aided in selection of solvents, understanding and controlling processes, and, in general, offered guidance where affinities among materials are of prime importance. To find the optimum solvent for a polymer using solubility parameters, it is most desirable to have the solubility parameters for the polymer. Matching the parameters of an already existing solvent or combination of solvents can be done, but does not necessarily optimize the new situation. The optimum depends on what is desired of the system. A solvent with highest possible affinity for the polymer is both expensive and probably not necessary.

Most coatings applications involve solvents safely within the solubility limit with a maximum of cheaper hydrocarbon solvent. Some safety is advised because temperature changes, potential variations in production, etc. can lead to a situation where solvent quality changes in an adverse manner. Balance of solvent quality on evaporation of mixed solvents is also necessary. Here again computer approaches are possible.

An oxygenated solvent frequently added to hydrocarbon solvent and which has been cost effective in increasing the very important hydrogen bonding solubility parameters has been *n*-butanol. The mixture of equal parts xylene and *n*-butanol can be used in conjunction with many polymers, but a third solvent, such as a ketone or ester, is often included in small amounts to increase the polar parameter/solvency of the mixture. Glycol ethers can also be added to hydrocarbon solvents with advantage, and the polar and hydrogen bonding parameters are higher than had *n*-butanol been added to the same concentration. There are many possibilities, and a solubility parameter approach is particularly valuable in quickly limiting the number of candidates.

Coalescing solvents in water-reducible coatings are often those with somewhat higher hydrogen bonding parameters than the polymer, which also means they are water soluble or have considerable water solubility. The distribution between the water phase and the dispersed polymer phase depends on the relative affinities for water and the polymer. Solvents which are not particularly water soluble will preferentially be found in the polymer phase. Such coalescing solvents may be preferred for applications to porous substrates, making certain they are where they are needed. Otherwise a water-soluble coalescing solvent would tend to follow the aqueous phase penetrating the substrate and not be available to do its job in the film itself.

When water evaporates the solvent must dissolve to some extent in the polymer to promote coalescence. This can be determined and adjusted by either increasing or decreasing the affinity for the polymer.

Amines are frequently added in water-reducible coatings to neutralize acid groups in polymers, thus providing a water-solubilizing amine salt. Amine in excess of that required for total neutralization acts like a solvent. Such amine salts have been characterized separately to demonstrate that they have higher solubility parameters than either (acetic) acid or organic bases [*42*]. These salts are hydrophilic and have very little affinity for coatings polymers, which means they are to be found in a stabilizing role in interfaces in the aqueous

TABLE 3—Hansen solubility parameters for selected liquids. The solvents in alphabetical order.

No.	Solvent	Dispersion	Polar	Hydrogen Bonding	Molar Volume
1	Acetaldehyde	14.7	8.0	11.3	57.1
2	Acetic acid	14.5	8.0	13.5	57.1
3	Acetic anhydride	16.0	11.7	10.2	94.5
4	*Acetone	15.5	10.4	7.0	74.0
5	Acetonitrile	15.3	18.0	6.1	52.6
6	*Acetophenone	19.6	8.6	3.7	117.4
7	Acrylonitrile	16.4	17.4	6.8	67.1
8	Allyl alcohol	16.2	10.8	16.8	68.4
9	Amyl acetate	15.8	3.3	6.1	148.0
10	Aniline	19.4	5.1	10.2	91.5
11	Anisole	17.8	4.1	6.7	119.1
12	Benzaldehyde	19.4	7.4	5.3	101.5
13	*Benzene	18.4	0.0	2.0	89.4
14	1.3-Benzenediol	18.0	8.4	21.0	87.5
15	Benzoic acid	18.2	6.9	9.8	100.0
16	Benzonitrile	17.4	9.0	3.3	102.6
17	Benzyl alcohol	18.4	6.3	13.7	103.6
18	Benzyl butyl phthalate	19.0	11.2	3.1	306.0
19	Benzyl chloride	18.8	7.1	2.6	115.0
20	Biphenyl	21.4	1.0	2.0	154.1
21	Bromobenzene	20.5	5.5	4.1	105.3
22	Bromochloromethane	17.3	5.7	3.5	65.0
23	Bromoform	21.4	4.1	6.1	87.5
24	1-Bromonaphtalene	20.3	3.1	4.1	140.0
25	Bromotrifluoromethane	9.6	2.4	0.0	97.0
26	Butane	14.1	0.0	0.0	101.4
27	1.3-Butanediol	16.6	10.0	21.5	89.9
28	*1-Butanol	16.0	5.7	15.8	91.5
29	2-Butanol	15.8	5.7	14.5	92.0
30	*Butyl acetate	15.8	3.7	6.3	132.5
31	Sec-butyl acetate	15.0	3.7	7.6	133.6
32	Butyl acrylate	15.6	6.2	4.9	143.8
33	Butylamine	16.2	4.5	8.0	99.0
34	Butyl lactate	15.8	6.5	10.2	149.0
35	Butyraldehyde	14.7	5.3	7.0	88.5
36	Butyric acid	14.9	4.1	10.6	110.0
37	*Gamma butyrolactone	19.0	16.6	7.4	76.8
38	Butyronitrile	15.3	12.4	5.1	87.3
39	Carbon disulfide	20.5	0.0	0.6	60.0
40	*Carbon tetrachloride	17.8	0.0	0.6	97.1
41	*Chlorobenzene	19.0	4.3	2.0	102.1
42	1-Chlorobutane	16.2	5.5	2.0	104.5
43	Chlorodifluoromethane	12.3	6.3	5.7	72.9
44	*Chloroform	17.8	3.1	5.7	80.7
45	3-Chloro-1-propanol	17.5	5.7	14.7	84.2
46	m-cresol	18.0	5.1	12.9	104.7
47	Cyclohexane	16.8	0.0	0.2	108.7
48	*Cyclohexanol	17.4	4.1	13.5	106.0
49	Cyclohexanone	17.8	6.3	5.1	104.0
50	Cyclohexylamine	17.2	3.1	6.5	113.8
51	Cyclohexylchloride	17.3	5.5	2.0	118.6
52	Cis-decahydronaphthalene	18.8	0.0	0.0	156.9
53	Trans-decahydronaphthalene	18.0	0.0	0.0	156.9
54	Decane	15.7	0.0	0.0	195.9
55	1-Decanol	17.5	2.6	10.0	191.8
56	*Diacetone alcohol	15.8	8.2	10.8	124.2
57	Dibenzyl ether	17.3	3.7	7.3	192.7
58	Dibutyl phthalate	17.8	8.6	4.1	266.0
59	Dibutyl sebacate	13.9	4.5	4.1	339.0
60	Dibutyl stearate	14.5	3.7	3.5	382.0
61	*o-dichlorobenzene	19.2	6.3	3.3	112.8
62	2.2-Dichlorodiethyl ether	18.8	9.0	5.7	117.2
63	Dichlorodifluoromethane	12.3	2.0	0.0	92.3
64	1.1-Dichloroethane	16.5	8.2	0.4	84.8
65	1.1-Dichloroethylene	17.0	6.8	4.5	79.0
66	Di-(2-chloro-isopropyl) ether	19.0	8.2	5.1	146.0
67	Dichloromonofluoromethane	15.8	3.1	5.7	75.4
68	1.2-Dichlorotetrafluoroethane	12.6	1.8	0.0	117.6
69	Di-iso-butyl carbinol	14.9	3.1	10.8	177.8
70	Diethanolamine	17.2	10.8	21.2	95.9
71	Diethylamine	14.9	2.3	6.1	103.2

TABLE 3—Hansen solubility parameters for selected liquids. The solvents in alphabetical order.

No.	Solvent	Dispersion	Polar	Hydrogen Bonding	Molar Volume
72	2-(Diethylamino)ethanol	14.9	5.8	12.0	133.2
73	Para-diethylbenzene	18.0	0.0	0.6	156.9
74	Diethyl carbonate	16.6	3.1	6.1	121.0
75	*Diethylene glycol	16.6	12.0	20.7	94.9
76	Diethylene glycol butyl ether acetate	16.0	4.1	8.2	208.2
77	Diethylene glycol hexyl ether	16.0	6.0	10.0	204.3
78	Diethylene glycol monobutyl ether	16.0	7.0	10.6	170.6
79	Diethylene glycol monoethyl ether	16.1	9.2	12.2	130.9
80	Diethylene glycol monomethyl ether	16.2	7.8	12.6	118.0
81	Diethylenetriamine	16.7	13.3	14.3	108.0
82	*Diethyl ether	14.5	2.9	5.1	104.8
83	Diethyl ketone	15.8	7.6	4.7	106.4
84	Diethyl phthalate	17.6	9.6	4.5	198.0
85	Diethyl sulfate	15.7	14.7	7.1	131.5
86	Diethyl sulfide	16.8	3.1	2.0	107.4
87	Di(isobutyl) ketone	16.0	3.7	4.1	177.1
88	Di(2-methoxyethyl) ether	15.7	6.1	6.5	142.0
89	N.N-dimethylacetamide	16.8	11.5	10.2	92.5
90	*Dimethylformamide	17.4	13.7	11.3	77.0
91	1.1-Dimethylhydrazine	15.3	5.9	11.0	76.0
92	Dimethyl phthalate	18.6	10.8	4.9	163.0
93	Dimethyl sulfone	19.0	19.4	12.3	75.0
94	*Dimethyl sulfoxide	18.4	16.4	10.2	71.3
95	Dioctyl phthalate	16.6	7.0	3.1	377.0
96	*1.4-Dioxane	19.0	1.8	7.4	85.7
97	Dipropylamine	15.3	1.4	4.1	136.9
98	*Dipropylene glycol	16.5	10.6	17.7	130.9
99	Dipropylene glycol methyl ether	15.5	5.7	11.2	157.4
100	Dodecane	16.0	0.0	0.0	228.6
101	Eicosane	16.5	0.0	0.0	359.8
102	Epichlorohydrin	19.0	10.2	3.7	79.9
103	Ethanethiol	15.7	6.5	7.1	74.3
104	*Ethanol	15.8	8.8	19.4	58.5
105	*Ethanolamine	17.0	15.5	21.2	59.8
106	*Ethyl acetate	15.8	5.3	7.2	98.5
107	Ethyl acrylate	15.5	7.1	5.5	108.8
108	Ethyl amyl ketone	16.2	4.5	4.1	156.0
109	Ethylbenzene	17.8	0.6	1.4	123.1
110	Ethyl bromide	16.5	8.0	5.1	76.9
111	2-Ethyl-1-butanol	15.8	4.3	13.5	123.2
112	Ethyl butyl ketone	16.2	5.0	4.1	139.0
113	Ethyl chloride	15.7	6.1	2.9	70.0
114	Ethyl chloroformate	15.5	10.0	6.7	95.6
115	Ethyl cinnamate	18.4	8.2	4.1	166.8
116	Ethylene carbonate	19.4	21.7	5.1	66.0
117	Ethylene cyanohydrin	17.2	18.8	17.6	68.3
118	Ethylenediamine	16.6	8.8	17.0	67.3
119	Ethylene dibromide	19.2	3.5	8.6	87.0
120	*Ethylene dichloride	19.0	7.4	4.1	79.4
121	*Ethylene glycol	17.0	11.0	26.0	55.8
122	Ethylene glycol butyl ether acetate	15.3	4.5	8.8	171.2
123	*Ethylene glycol monobutyl ether	16.0	5.1	12.3	131.6
124	*Ethylene glycol monoethyl ether	16.2	9.2	14.3	97.8
125	Ethylene glycol monoethyl ether acetate	15.9	4.7	10.6	136.1
126	*Ethylene glycol monomethyl ether	16.2	9.2	16.4	79.1
127	Ethylene glycol monomethyl ether acetate	15.9	5.5	11.6	121.6
128	Ethyl formate	15.5	8.4	8.4	80.2
129	2-Ethyl hexanol	15.9	3.3	11.8	156.6
130	Ethyl lactate	16.0	7.6	12.5	115.0
131	*Formamide	17.2	26.2	19.0	39.8
132	Formic acid	14.3	11.9	16.6	37.8
133	Furan	17.8	1.8	5.3	72.5
134	Furfural	18.6	14.9	5.1	83.2
135	Furfuryl alcohol	17.4	7.6	15.1	86.5
136	Glycerol	17.4	12.1	29.3	73.3
137	Heptane	15.3	0.0	0.0	147.4
138	Hexadecane	16.3	0.0	0.0	294.1
139	Hexamethylphosphoramide	18.5	8.6	11.3	175.7
140	*Hexane	14.9	0.0	0.0	131.6
141	Hexylene glycol	15.7	8.4	17.8	123.0
142	Isoamyl acetate	15.3	3.1	7.0	148.8

TABLE 3 Continued—Hansen solubility parameters for selected liquids. The solvents in alphabetical order.

No.	Solvent	Dispersion	Polar	Hydrogen Bonding	Molar Volume
143	Isobutyl acetate	15.1	3.7	6.3	133.5
144	Isobutyl alcohol	15.1	5.7	15.9	92.8
145	Isobutyl isobutyrate	15.1	2.9	5.9	163.0
146	Isooctyl alcohol	14.4	7.3	12.9	156.6
147	Isopentane	13.7	0.0	0.0	117.4
148	*Isophorone	16.6	8.2	7.4	150.5
149	Isopropyl palmitate	14.3	3.9	3.7	330.0
150	Mesitylene	18.0	0.0	0.6	139.8
151	Mesityl oxide	16.4	6.1	6.1	115.6
152	Methacrylonitrile	15.3	10.8	3.6	83.9
153	*Methanol	15.1	12.3	22.3	40.7
154	o-Methoxyphenol	18.0	8.2	13.3	109.5
155	Methyl acetate	15.5	7.2	7.6	79.7
156	Methyl acrylate	15.3	9.3	5.9	89.7
157	Methylal	15.0	1.8	8.6	169.4
158	Methyl amyl acetate	15.2	3.1	6.8	167.4
159	Methyl butyl ketone	15.3	6.1	4.1	123.6
160	Methyl chloride	15.3	6.1	3.9	55.4
161	Methylcyclohexane	16.0	0.0	1.0	128.3
162	*Methylene dichloride	18.2	6.3	6.1	63.9
163	Methylene diiodide	17.8	3.9	5.5	80.5
164	Methyl ethyl ketone	16.0	9.0	5.1	90.1
165	Methyl isoamyl ketone	16.0	5.7	4.1	142.8
166	Methyl isobutyl carbinol	15.4	3.3	12.3	127.2
167	*Methyl isobutyl ketone	15.3	6.1	4.1	125.8
168	Methyl methacrylate	17.5	5.5	4.3	106.5
169	1-Methylnaphthalene	20.6	0.8	4.7	138.8
170	Methyl oleate	14.5	3.9	3.7	340.0
171	2-Methyl-1-propanol	15.1	5.7	15.9	92.8
172	*Methyl-2-pyrrolidone	18.0	12.3	7.2	96.5
173	Methyl salicylate	16.0	8.0	12.3	129.0
174	Morpholine	18.8	4.9	9.2	87.1
175	Naphtha.high-flash	17.9	0.7	1.8	181.8
176	Naphthalene	19.2	2.0	5.9	111.5
177	*Nitrobenzene	20.0	8.6	4.1	102.7
178	*Nitroethane	16.0	15.5	4.5	71.5
179	*Nitromethane	15.8	18.8	5.1	54.3
180	1-Nitropropane	16.6	12.3	5.5	88.4
181	*2-Nitropropane	16.2	12.1	4.1	86.9
182	Nonane	15.7	0.0	0.0	179.7
183	Nonyl phenol	16.5	4.1	9.2	231.0
184	Nonyl phenoxy ethanol	16.7	10.2	8.4	275.0
185	Octane	15.5	0.0	0.0	163.5
186	Octanoic acid	15.1	3.3	8.2	159.0
187	1-Octanol	17.0	3.3	11.9	157.7
188	2-Octanol	16.1	4.9	11.0	159.1
189	Oleic acid	14.3	3.1	5.5	320.0
190	Oleyl alcohol	14.3	2.6	8.0	316.0
191	Pentane	14.5	0.0	0.0	116.2
192	2.4-Pentanedione	17.1	9.0	4.1	103.1
193	1-Pentanol	15.9	4.5	13.9	108.6
194	Perfluoro(dimethylcyclohexane)	12.4	0.0	0.0	217.4
195	Perfluoroheptane	12.0	0.0	0.0	227.3
196	Perfluoromethylcyclohexane	12.4	0.0	0.0	196.0
197	Phenol	18.0	5.9	14.9	87.5
198	Bis-(m-phenoxyphenyl) ether	19.6	3.1	5.1	373.0
199	1-Propanol	16.0	6.8	17.4	75.2
200	2-Propanol	15.8	6.1	16.4	76.8
201	Propionitrile	15.3	14.3	5.5	70.9
202	Propylamine	16.9	4.9	8.6	83.0
203	Propyl chloride	16.0	7.8	2.0	88.1
204	*Propylene carbonate	20.0	18.0	4.1	85.0
205	*Propylene glycol	16.8	9.4	23.3	73.6
206	Propylene glycol monobutyl ether	15.3	4.5	9.2	132.0
207	Propylene glycol monoethyl ether	15.7	6.5	10.5	115.6
208	Propylene glycol monoisobutyl ether	15.1	4.7	9.8	132.2
209	Propylene glycol monomethyl ether	15.6	6.3	11.6	93.8
210	Propylene glycol monophenyl ether	17.4	5.3	11.5	143.2
211	Propylene glycol monopropyl ether	15.8	7.0	9.2	130.3
212	Pyridine	19.0	8.8	5.9	80.9
213	2-Pyrolidone	19.4	17.4	11.3	76.4

TABLE 3 Continued—Hansen solubility parameters for selected liquids. The solvents in alphabetical order.

No.	Solvent	Dispersion	Polar	Hydrogen Bonding	Molar Volume
214	Quinoline	19.4	7.0	7.6	118.0
215	Stearic acid	16.3	3.3	5.5	326.0
216	Styrene	18.6	1.0	4.1	115.6
217	Succinic anhydride	18.6	19.2	16.6	66.8
218	1.1.2.2-Tetrabromoethane	22.6	5.1	8.2	116.8
219	1.1.2.2-Tetrachloroethane	18.8	5.1	9.4	105.2
220	Tetrachloroethylene	19.0	6.5	2.9	101.1
221	Tetraethylorthosilicate	13.9	0.4	0.6	224.0
222	*Tetrahydrofuran	16.8	5.7	8.0	81.7
223	Tetrahydronaphthalene	19.6	2.0	2.9	136.0
224	Tetramethylurea	16.7	8.2	11.0	120.4
225	*Toluene	18.0	1.4	2.0	106.8
226	Tributyl phosphate	16.3	6.3	4.3	345.0
227	Trichlorobiphenyl	19.2	5.3	4.1	187.0
228	1.1.1-Trichloroethane	16.8	4.3	2.0	99.3
229	*Trichloroethylene	18.0	3.1	5.3	90.2
230	Trichlorofluoromethane	15.3	2.0	0.0	92.8
231	1.1.2-Trichlorotrifluoroethane	14.7	1.6	0.0	119.2
232	Tricresyl phosphate	19.0	12.3	4.5	316.0
233	Tridecyl alcohol	14.3	3.1	9.0	242.0
234	Triethanolamine	17.3	22.4	23.3	133.2
235	Triethylamine	17.8	0.4	1.0	138.6
236	Triethyleneglycol	16.0	12.5	18.6	114.0
237	Triethylene glycol monooleyl ether	13.3	3.1	8.4	418.5
238	Triethylphosphate	16.7	11.4	9.2	171.0
239	Trifluoroacetic acid	15.6	9.9	11.6	74.2
240	Trimethylbenzene	17.8	0.4	1.0	133.6
241	2.2.2.4-Trimethylpentane	14.1	0.0	0.0	166.1
242	2.2.4-Trimethyl-1.3-pentanediol M.I. butyral	15.1	6.1	9.8	227.4
243	Trimethylphosphate	16.7	15.9	10.2	115.8
244	Water	15.5	16.0	42.3	18.0
245	Xylene	17.6	1.0	3.1	123.3
246	o-xylene	17.8	1.0	3.1	121.2

*Indicates use in author's standard set of test solvents.

phase, still being attached to the polymer. Electrostatic repulsion contributes to stability as well.

Surface active agents, whether nonionic or ionic, are also to be found where the affinities of the respective parts of their molecules dictate their placement. The hydrophilic end with a high hydrogen bonding parameter will be in the aqueous phase, and the hydrophobic end will seek out an environment where energy differences are lowest.

Increases in temperature lead to lower hydrogen bonding parameters, especially. For this reason solvents with high hydrogen bonding parameters, such as glycols, glycol ethers, and alcohols, become better solvents for most polymers at higher temperatures. This can markedly affect hot-room stability in water-reducible coatings, for example, since more of the solvent will partition to the polymer phase, which swells, becomes more fluid, and has altered affinities for stabilizing surface active agents, for example. They may dissolve too readily in the dispersed polymer. Carefully controlled, these temperature effects are an advantage in water-reducible, oven-cured coatings, leading to higher film integrity.

A simple approach to many practical problems is to make a two-dimensional plot of polar versus hydrogen bonding parameters with a circle (or estimated circle) for the polymer in question. One can plot the points for potential solvents and quickly arrive at a starting composition for an experiment. This can subsequently be adjusted if necessary. It should also be kept in mind that cyclic solvents generally have higher nonpolar parameters than aliphatic solvents.

A long list of applications, in coatings and elsewhere, was provided as early as 1975 in a review article by Barton [*43*]. Many applications are given in Table 6 and in the present discussion to give an idea of what can be studied systematically using this concept. More recent references and varied applications can be found in Refs *3*, *4*, and *44*.

Beerbower [*44*] has given many of the more theoretical applications for solubility parameters including correlations of the Rehbinder effect of crushing strength of aluminum oxide under various liquids, the work of adhesion for liquids on mercury, the Joffe effect of the consequences of immersion in various liquids on the fracture strength of soda-lime glass, and correlations of friction on polyethylene treated with fuming sulfuric acid $H_2SO_4 + SO_3$ [*44*].

Direct and practical applications of solubility parameters in coatings have included their use as an aid in the selection of solvents and solvent blends for many years. Most solvent suppliers and frequent solvent users have computer programs for this purpose, although as noted above, such programs are not an absolute necessity. Reformulation to meet environmental requirements is especially important in this respect since one can quickly evaluate which of the alternatives is most likely to meet the given requirements. This includes reducing amounts of volatile organic solvent (VOC) and often involves mixtures.

The main thing to remember in solvent selection using solubility parameters is that the resultant values for mixtures can be estimated from volume fraction averages for each

TABLE 4—Solubility parameters for polymers.

	D	P	H	R
Cellulose acetobutyrate				
Cellit BP-300[a]	16.6	12.0	6.7	10.2
Cellulose acetate				
Cellidora A[a]	18.2	12.4	10.8	7.4
Ethyl cellulose				
Ethocel HE 10 ind[b]	17.9	4.3	3.9	5.9
Ethocel Std 20 ind[b]	20.1	6.9	5.9	9.9
Epoxy				
Araldite DY 025	14.0	7.4	9.4	13.7
Epikote 828	21.3	14.2	6.1	17.7
Epikote 1001	18.1	11.4	9.0	9.1
Epikote 1004	17.4	10.5	9.0	7.9
Epikote 1007	21.0	11.1	13.4	11.7
Epikote 1009	18.9	9.6	10.7	7.8
Phenoxy PKHH	23.4	7.2	14.8	14.9
Epoxy curing agents				
Versamid 100	23.8	5.3	16.2	16.1
Versamid 115	20.3	6.6	14.1	9.6
Versamid 125	24.9	3.1	18.7	20.3
Versamid 140	26.9	2.4	18.5	24.0
Polyurethane				
Desmophen 651	17.7	10.6	11.6	9.5
Desmophen 800	19.1	12.2	9.9	8.0
Desmophen 850[a]	21.1	14.6	12.0	16.2
Desmophen 1100	16.0	13.1	9.2	11.4
Desmophen 1150	20.6	7.8	11.6	13.1
Desmophen 1200	19.4	7.4	6.0	9.8
Desmophen 1700	17.9	9.6	5.9	8.2
Desmolac 4200	18.7	9.6	9.9	8.2
Macrynal SM 510N	19.9	8.1	6.0	9.8
Phenolic resins				
Super Beckacite 1001[a]	22.7	6.4	8.2	19.4
Phenodur 373 U[a]	19.3	11.4	14.3	12.4
Hydrocarbon resins				
Piccolyte S-100[a]	16.1	0.4	2.8	8.4
Piccopale 110[a]	17.2	1.2	3.5	6.4
Piccoumarone 450 L[a]	19.0	5.4	5.6	9.4
Styrene-butadiene elastomer (SBR)				
Polysar 5630[a]	17.2	3.3	2.6	6.4
Acrylonitrile-butadiene elastomer				
Hycar 1052[a]	18.2	8.6	4.1	9.4
Polybutadiene				
Buna Hüls B-10[a]	17.1	2.2	3.3	6.4
Polyisoprene				
Cariflex IR 305[a]	16.2	1.4	−0.8	9.4
Polyisobutylene				
Lutonal IC/1203[a]	14.2	2.5	4.6	12.4
Lutonal I60	16.9	2.5	4.0	7.2
Polyvinylbutyl ether	17.4	4.3	8.4	7.4
Lignin powder[a]	19.7	14.3	14.7	11.4
Modaflow Multiflow	16.1	3.7	7.9	8.9
Polyvinylchloride				
Vipla KR[a]	17.2	7.4	8.2	3.4

TABLE 4 Continued—Solubility parameters for polymers.

	D	P	H	R
Chlorparaffin				
Cereclor 70	20.0	8.3	6.8	9.8
Chlorparaffin 40	17.0	7.6	7.9	11.9
Chlorinated rubber				
Pergut S 5	17.4	9.5	3.8	10.0
Allopren R 10	17.4	4.3	3.9	6.1
Chlorinated polypropylene				
Parlon P 10[a]	19.8	6.2	5.3	10.4
Chlorosulfonated polyethylene				
Hypalon 20[b]	18.1	3.4	4.9	3.6
Hypalon 30[b]	18.2	4.7	2.0	5.0
Cyclized rubber				
Alpex[b]	19.9	0.0	0.0	9.4
Nitrocellulose				
1/2-*sec*-Nitrocellulose H 23[a]	15.1	14.4	8.6	11.2
Rosin derivatives				
Cellolyn 102[a]	21.2	0.9	8.3	15.4
Pentalyn 255[a]	17.2	9.2	14.0	10.4
Pentalyn 830[a]	19.6	5.7	10.7	11.4
Ester Gum 8L[a]	19.2	4.6	7.6	10.4
Polyamide				
Versamid 930[a]	17.0	−1.9	14.6	7.4
Versamid 961	18.9	9.6	11.1	6.2
Versamid 965	20.4	0.4	14.0	12.9
Isocyanate				
Desmodur L	17.5	11.3	5.9	8.5
Demodur N[a]	17.6	10.0	3.7	9.3
Suprasec F-5100[a]	19.7	12.9	12.8	11.4
Polyvinylbutyral				
Mowithal B 30 H	18.6	12.9	10.3	8.3
Mowithal B 60 H	20.2	11.2	13.3	11.2
Butvar B 76[a]	18.2	4.3	12.7	10.4
Polyacrylate				
Lucite 2042[a]	17.2	9.4	3.9	10.4
Lucite 2044	16.2	6.8	5.7	9.1
Plexigum MB 319	18.6	10.8	4.1	11.5
Plexigum M 527	18.4	9.4	6.5	10.7
PMMA[a]	18.2	10.3	7.7	8.4
Polyvinylacetate				
Mowilith 50[a]	20.5	11.0	9.4	13.4
Polystyrene				
Polystyren LG[a]	20.8	5.6	4.2	12.4
Vinylchloride/copolymers				
Laroflex MP 45	18.4	8.4	5.8	9.0
Vilit MB 30	20.0	8.3	6.7	9.4
Vilit MC 31	20.0	8.3	6.7	9.4
Vilit MC 39	18.4	7.6	6.7	6.8
Vinylite VAGD	17.1	10.4	6.5	7.5
Vinylite VAGH	16.5	10.9	6.4	7.7
Vinylite VMCA	17.7	11.1	6.9	8.7
Vinylite VMCC	17.6	11.1	6.8	8.8
Vinylite VMCH	17.6	11.1	6.4	8.6
Vinylite VYHH	17.4	10.2	5.9	7.8
Vinylite VYLF	18.1	10.3	4.2	8.3

TABLE 4 Continued—Solubility parameters for polymers.

	D	P	H	R
Binders in solution				
Alkyds and polyesters				
Alftalat AC 366	18.6	10.0	5.0	10.4
Alftalat AM 756	23.0	2.2	4.2	16.9
Alftalat AN 896	22.9	15.2	7.6	18.1
Alftalat AN 950	22.6	13.8	8.1	17.1
Alftalat AT 316	20.5	9.3	9.1	12.4
Alftalat AT 576	19.2	5.3	6.3	11.9
Alkydal F 261 HS	23.6	1.0	7.6	19.0
Alkydal F 41	20.6	4.6	5.5	12.6
Duroftal T 354	17.3	4.2	7.9	9.3
Dynapol L 812	22.6	13.1	5.8	16.8
Dynapol L 850	20.0	6.2	7.0	9.5
Plexal C-34[a]	18.1	9.0	4.8	10.4
Soalkyd 1935-EGAX	18.0	11.6	8.5	9.0
Vesturit BL 908	18.8	12.0	6.0	11.5
Vesturit BL 915	17.7	13.0	7.6	11.5
Amino resins				
BE 370	20.7	6.1	12.7	14.8
Beetle 681	22.2	−0.4	10.1	18.4
Cymel 300[a]	19.9	8.3	10.4	14.4
Cymel 325	25.5	15.2	9.5	22.2
Dynomin MM 9	18.8	14.0	12.3	10.5
Dynomin UM 15	19.9	15.8	13.4	11.7
Soamin M 60	15.9	8.1	6.5	10.6
Synresen A 560	22.1	5.0	11.3	15.5
Plastopal H[a]	20.3	8.1	14.6	12.4
Uformite MX-61	22.7	2.8	5.4	16.2
Acrylate resins				
Uracron 15	19.2	7.7	5.7	10.6
Paraloid P 400	19.2	9.6	9.3	12.2
Paraloid P 410	19.6	9.1	6.8	12.2
Paraloid experimental resin QR 954	18.4	9.8	10.0	12.4
Silicone resins				
Baysilon UD 125	19.4	9.9	10.1	6.9
Wacker 190 F	16.6	1.9	8.0	8.0
Additional Special Data				
DEN 438 (Dow epoxy novolak)	20.3	15.4	5.3	15.1
DEN 444 (Dow epoxy novolak)	19.5	11.6	9.3	10.0
Zink silicate (CR)—Chemical resistance	23.5	17.5	16.8	15.6
2-Comp epoxy (CR)—Chemical resistance	18.4	9.4	10.1	7.0
Polyvinylidine fluoride	17.0	12.1	10.2	4.1
Coal tar pitch	18.7	7.5	8.9	5.8
PA6 polyamide chemical resistance	17.0	3.4	10.6	5.1
PA66 polyamide solubility	17.4	9.8	14.6	5.1
PA11 polyamide chemical resistance	17.0	4.4	10.6	5.1
Cellophane swelling	16.1	18.5	14.5	9.3
EVOH—solubility (ethylenevinyl alcohol)	20.5	10.5	12.3	7.3

Note: D = dispersion; P = permanent dipoles; H = hydrogen bonding; R = interaction radius.

[a]Taken from Hansen, C. M., "Solubility in the Coatings Industry," *Färg och Lack*, Vol. 17, No. 4, 1971, pp. 69–77.

[b]Calculated from solubility data in *Polymer Handbook*, 2nd ed., John Wiley & Sons, Inc., New York, 1975.

solubility parameter component. Solvent quality can be adjusted by the RED number concept or graphically as described above.

A computer search for nearest neighbors for a given single solvent has been used many times to locate alternates. A similar application is to predict which other solvents will probably be aggressive to a chemically resistant coating where very limited data have indicated a single solvent or two are somewhat aggressive. A nearest neighbor search involves calculation of the quantity R_s for a whole database, for example, and then arranging the printout in RED number order with the potentially most aggressive at the top of the list. Solvents with RED less than 1.0 are "good" and easily recognized.

In many cases a marginal solvent is desired, in which case RED numbers just under 1.0 will be sought. Marginal solvent quality will ensure that polymer adsorbed onto pigment surfaces has little reason to dissolve away from that surface where it is desired as a stabilizing factor in the product. The solvent in this case should have a RED number for the pigment surface greater than 1.0 to aid in the planned affinity approach to pigment dispersion stability. A sketch of the optimum relations is given in Fig. 4, where the marginal solvent is Number 1. Solvent 2 would probably be too expensive and, in addition, will probably dissolve the polymer too well. In special applications this extended polymer chain configuration is desirable, but a solid anchor to the pigment surface is required. A good anchor has high affinity for the pigment surface and marginal or no affinity for the solvent. Solvent 3

TABLE 5—List of suppliers and trademarks for paint binders and polymers.

Suppliers	Trademarks
Bayer (D)	Cellit, Desmophen, Desmolac, Pergut, Cellidora, Desmodur, Baysilon Alkydal
Hercules (USA)	Piccolyte, Cellolyn, Pentalyn, Ester Gum, Parlon
Ciba-Geigy	Araldite
Shell (D)	Epikote, Cariflex
Union Carbide (USA)	Vinylite, Phenoxy
Hoechst (D)	Macrynal, Phenodur, Alpex, Mowithal, Alftalat, Mowilith
Reichhold (CH)	Super Beckasite, Uformite
Polymer Corp. (CAN)	Polysar
Goodrich (USA)	Hycar
Hüls (D)	Vilit, Vesturit, Buna Hüls
BASF (D)	Lutonal, Laroflex, Plastopal, Polystyren
Monsanto (USA)	Modaflow, Multiflow, Butvar
Montecatini Edison (I)	Vipla
ICI (GB)	Cereclor, Allopren, Suprasec
Du Pont (USA)	Lucite
Hagedorn (D)	1/2-sec. nitrocellulose H 23
Röhm (D)	Plexigum
Rohm and Haas (USA)	Paraloid
Dynamit Nobel (D)	Dynapol
SOAB (S)	Soamin
BIP Chemicals (GB)	Beetle
Dyno Cyanamid (N)	Dynomin
DSM Resins (S)	Uracron
Reichhold Chemie (CH)	Super Beckasite, Uformite
Wacker (D)	Wacker
Dow Chemical (CH)	Ethocel
Cray Valley Prod. (GB)	Versamid
W. Biesterfeld (D)	Chlorparaffin
Synres (NL)	Synresen
American Cyanamide (USA)	Cymel
Polyplex (DK)	Plexal
Pennsylvania Industrial Chemical Corp. (USA)	Piccopal, Piccoumarone

TABLE 6—Examples of the use of the solubility parameter.

Activity coefficients
Aerosol formulation
Biological materials and compatibility
Chromatography
Coal solvent extraction
Compressed gases
Cosmetics
Cryogenic solvents
Dispersion
Dyes
Emulsions
Gas-Liquid solubility
Grease removal
Membrane permeability and swelling
Paint film appearance
Pharmaceutical
Pigments
Plasticizers, polymers, resins
Plasticization
Polymer and plasticizer compatibility
Printing ink
Reaction rate of radical polymerization
Resistance of plastics to solvents
Rubber blends
Solid surface characterization—organic and inorganic
Solid surface modification
Solvent extraction
Solvent formulation, environmental aspects
Surface tension
Urea-water solutions
Vaporization of plasticizers
Viscosity of polymer systems
Water-based polymer systems, coalescents

would adsorb onto the pigment surface preferentially, and pigment dispersion stability will be poor. Pigments have been characterized by long-time suspension studies where some solvents will suspend the fines for days, months, or years, while others of similar viscosity yield rapid settling. The suspending solvents are the "good" ones and can be used to define a sphere for surface wetting/adsorption.

In other cases better matches between solvent and polymer solubility parameters are required. This is true when two polymers are mixed and one of them precipitates. This is most likely the polymer with larger molecular weight, and it must be dissolved better. Lower RED numbers with respect to this polymer are desired, while still maintaining affinity for the other polymer. Miscible blends of two polymers have been found using a solvent mixture composed exclusively of nonsolvents. This is demonstrated schematically in Fig. 5, where it can be seen that different percentage blends of Solvents 1 and 2 will have different relative affinities for the polymers. No other alternative theory of polymer solution thermodynamics can duplicate this predictive ability. Polymer miscibility is enhanced by larger overlapping solubility regions for the polymers as sketched in Fig. 6. Polymers A and B should be compatible, while C will not be. Such a systematic analysis allows modification of a given polymer to provide more overlap and enhanced compatibility. The advantages of a copolymer containing the monomers of A or B and C should also be evident. Such a copolymer will essentially couple the system together.

Van Dyk et al. [*45*] have correlated the inherent viscosity of polymer solutions with the solubility parameter. This is interesting in that the solubility parameter is a thermodynamic consideration, while the viscosity is a kinetic phenomena. Solvents with higher affinities give greater polymer chain extension in solution, and the inherent viscosity—the solution viscosity divided by the solvent viscosity at polymer concentrations approaching zero—is an expression reflecting polymer chain extension in solution. Higher intrinsic viscosities were found for solvents with solubility parameters nearest the polymer solubility parameters.

The use of supercritical gases as solvents has become more common in recent years. Space limitations prevent going into the details of these developments. It should be noted, however, that when a gas is compressed its cohesive energy density increases. This means that nonpolar gases with their low nonpolar solubility parameters can begin to dissolve given organic materials which otherwise have solubility parameters which are too high. Increasing the nonpolar solubility parameter of the gas by increasing the pressure causes a

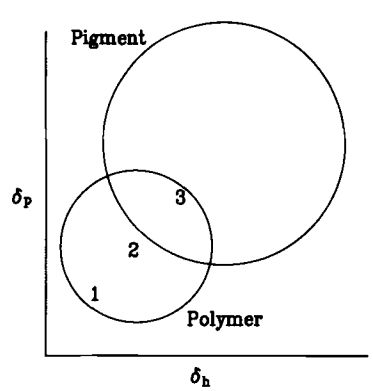

FIG. 4–Solubility parameter relations for optimum pigment dispersion stability.

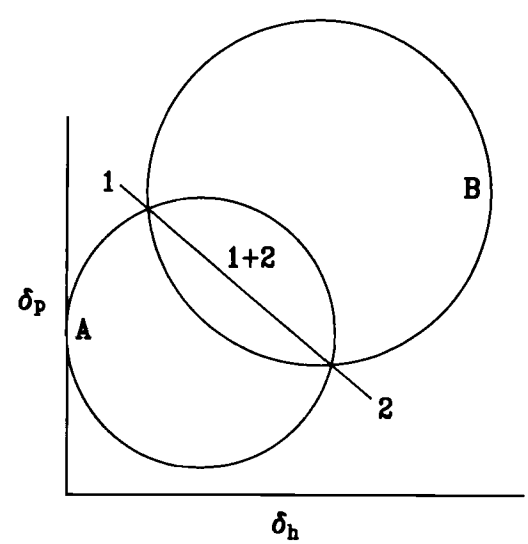

FIG. 5–Solubility relations for polymer mixtures can be quickly evaluated to ensure solution stability. Even mixtures of nonsolvents can be systematically used to regulate solution behavior.

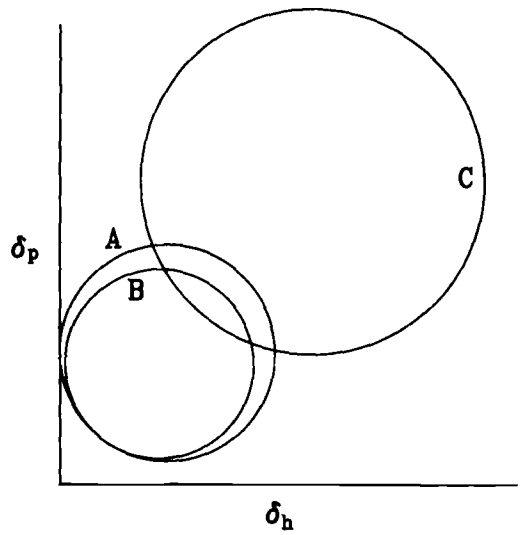

FIG. 6–Schematic representation showing expected miscibility of Polymers A and B with each other but not with Polymer C.

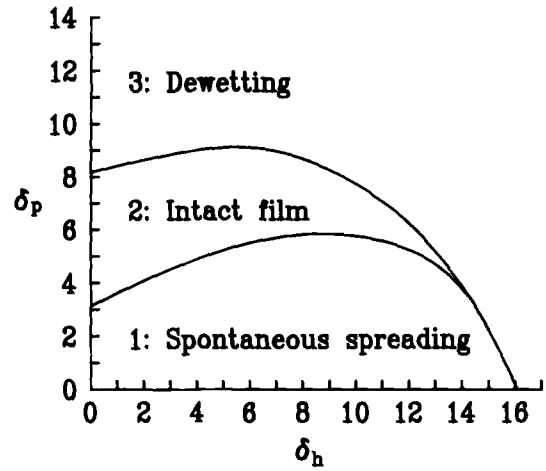

FIG. 7–Schematic diagrams showing surface energy/contact angle characterizations using the Hansen solubility parameters (cohesion energy parameters).

closer match with the corresponding parameter for potential solutes. Similar behavior is found for polar gases such as carbon dioxide. The prevailing pressure and temperature conditions determine its cohesive energy density and changes in pressure or temperature change solubility relations for this reason. Whereas nonpolar gases are most suitably used for relatively nonpolar solutes, carbon dioxide—and in principle other polar gases—are most suitably used in connection with more polar solutes. The solubility parameters for carbon dioxide have been reported [*46*] based on the room temperature solubility of the gas in different liquids (δ_d, δ_p, δ_h equal to 15.3, 6.9, 4.1). These parameters resemble those of a higher ketone.

Pigment wetting/suspension characteristics have been presented earlier [*2,4,10*]. Mixtures of nonsuspending solvents could also be found which, when admixed, provided predictably higher affinity and suspension of pigment particles for prolonged periods of time. An exceptionally clear demonstration of pigment adsorption properties is given in Ref *4* where a triangular plot of the three partial parameters shows the clearly different adsorption properties of untreated zinc oxide powder and organic phosphate surface-treated zinc oxide powder. This triangular approach to plotting was developed by Teas [*41*].

Other surface characterizations have also been given for surfaces such as coatings and metal substrates [*17,18*]. These characterizations have been of the type sketched in Fig. 7. Such cohesive energy plots can lead to systematic modifications of systems to improve adhesion. It might be added parenthetically that equal information can be obtained from plots of the cosine of the contact angle versus the solubility parameter as for plots of these same data versus liquid surface tension [*17*]. The energy information obtained in these types of studies, the critical surface tension, corresponds to the condition of RED equal to 1.0, with a solubility parameter approach, that is, marginal affinity.

The list of applications has recently been expanded to include correlations of the breakthrough times for common types of chemical protective clothing such as butyl rubber, nitrile rubber, plasticized polyvinyl chloride, neoprene, Viton rubber, polyvinyl alcohol, etc. [*47*]. Figure 8 shows the importance of combined use of the RED number and molecular volume in correlating 3-h breakthrough times for a fluoropolymer chemical protective product [*48*]. Monomers with terminal double bonds diffuse more rapidly than comparisons with non-double-bonded molecules of similar size and solubility parameter would have predicted. The smaller cross section at the end of the molecule reminds one of a nail, and the preferred direction and relative rapidity of transport become easily understandable.

In addition it should be noted that even biological materials, some of which have interest for coatings applications and use, have been assigned Hansen solubility parameters [*49*]. These include keratin (which relates to skin permeation), fat, sucrose, blood serum and zein (which are proteins), urea, lignin (wood penetration), and chlorophyll (which closely resembles lignin) [*46,49*]. The characterization of other biological materials is also possible, of course.

Even inorganic salts have been characterized by solubility parameters [*50*]. The practice of dissolving polymers in solutions of organic liquids and inorganic salts can thus be explained by the solubility parameter. A solubility parameter correlation of the chemical resistance of an inorganic zinc silicate coating is reported in Table 4. Finally it might be noted that Hildebrand presented a chapter on the solubility parameters of metals [*1*]. Unfortunately we do not often coat metal, but rather metal oxides, for which no solubility parameter work has been reported.

CONCLUSION

The background and many uses of the solubility parameter concept have been described in detail. Tables of solubility parameters for many liquids and polymers have been presented. Systematic use of solubility, swelling, or permeation

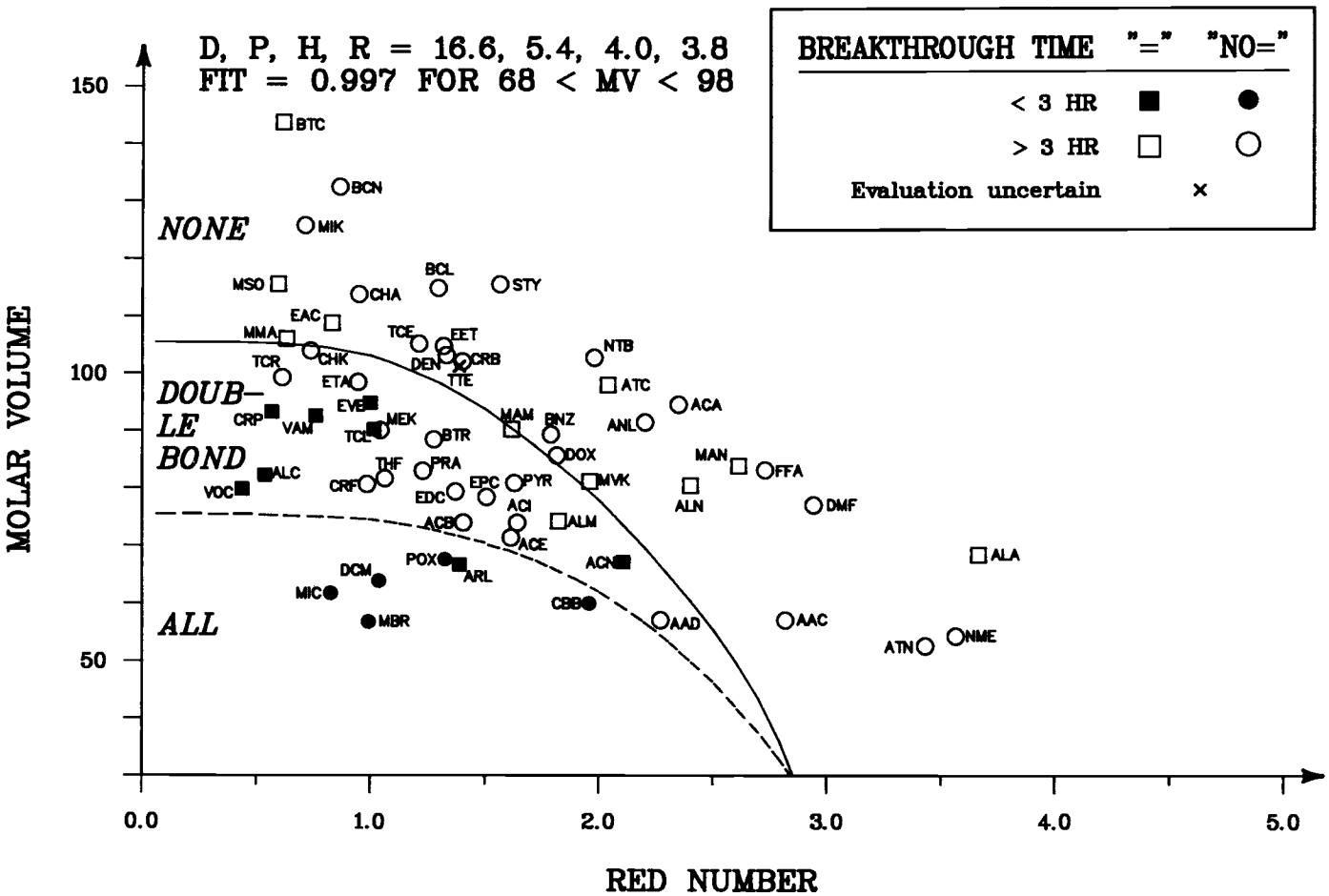

FIG. 8–Effects of molecular size (molar volume) and affinity (RED number) on the breakthrough time of Challenge 5100 [*48*].

data for polymers allows their characterization by these same cohesive energy parameters. Surfaces can also be characterized using these same parameters. This provides data for optimizing solvent selection, improving compatibility, and enhancing pigment dispersion and adhesion. When all of the materials involved in a given product and application can be characterized with the same energy parameters, the possibility exists to predict interactions among them, even in complicated situations. Methods for estimating the three Hansen solubility parameters have been given with as much detail as has been possible to ensure their more uniform use in the future. It has not been possible to deal with all the primarily theoretical problems with the solubility parameter concept. Some of these are dealt with in the literature cited, most notably in Refs *3*, *4*, *12*, and *20*.

A simple approach is described to understand affinities in such varied materials as gases, liquids, polymers, biological materials, surfaces, organic and inorganic coatings, inorganic salts, and metals. An appeal is made to the scientific community to expand research on this seemingly universal approach.

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Part 9: Films for Testing

36

Cure: The Process and Its Measurement

by Thomas J. Miranda[1]

INTRODUCTION

One of the most critical, and often misunderstood properties of a coating is cure and its measurement. The optimum physical and chemical properties of a coating depend largely on proper curing conditions. For example, a thermosetting acrylic polymer when applied to a panel and dried without curing will be brittle and have poor solvent resistance and low hardness. When properly cured, the film properties will change dramatically and the properties which were designed into the coating become apparent. Similarly, an oil-based paint will be soft and tacky and slowly become hard and scratch resistant as its cure develops. To appreciate the scope of the material in this chapter, it may be well to review a few film-forming mechanisms, polymer fundamentals, and some background into the development of tests and what they mean.

Background and Film Formation

Polymers

A polymer is a high-molecular-weight interreaction product of related polyfunctional molecules [*1*]. The term *polymer* is derived from the Greek poly (many) and mer (part). Polymers are formed from monomers (mono = one) (mer = part) by a process of polymerization. Polymers consist of long chains of macromolecules with molecular weights of a few thousand up to many millions. For example, ultrahigh-molecular-weight polyethylene may have a molecular weight of 4 to 6 million, while alkyds have molecular weights of a few thousand. The concept of macromolecules was developed by Herman Staudinger in 1920 [*2*]. Staudinger's theory was supported by the work of Wallace Carothers, who introduced the concept of functionality and the distinction between thermoplastic and thermosetting polymers [*3*].

There are two types of polymers: addition and condensation. Addition polymers have high molecular weight and are characterized by fast chain reaction syntheses that are exothermic and initiated by free radical, coordination polymerization, cationic, group transfer, or anionic mechanisms. Free radical-initiated polymerization is initiated by incorporation of a free radical producer such as benzoyl peroxide which decomposes with heat to form free radicals, which in turn initiate polymerization. Coordination polymerization is initiated by complex initiator systems such as those used to polymerize ethylene or propylene and sometimes referred to as Ziegler-Natta catalysts made from an organometal and an inorganic compound like titanium tetrachloride. Cationic initiation can be done using Lewis acids such as aluminum chloride or boron trifluoride and are usually carried out at low temperatures. Butyl rubber is made by such a process. Group transfer is a relatively new type of polymer initiation, while the anionic processes use organometals (butyl lithium) to produce polymers. Block polymers are made by anionic processes. Condensation polymers have lower molecular weight than addition types and are produced by stepwise addition with elimination of water as a byproduct and require a longer time to synthesize using an endothermic process [*4*].

Cure Concept and Illustrations

We can simplistically illustrate the concept by considering a long chain polymer (thermoplastic) as a wire fence with a number of strands (Fig. 1) such as used on a farm. An individual can pass through the fence by spreading the strands apart, and standing on the fence will cause the strand to sag or elongate. If, however, we take that fence and lace it with wire such that a hogwire fence is produced, then we see the changes in the physical properties of this (thermoset) fence. First, it would be difficult to pass through the fence; second, one can stand on the fence since it is stronger and will not yield as would the single strand fence. If one considers the ability to pass through the fence as solvent action, it is easy to visualize how solvent molecules can permeate and dissolve a thermoplastic polymer, but difficult or impossible to dissolve a thermoset polymer. In fact, a thermoset polymer will tend to swell, such as a rubber band in a hydrocarbon solvent. This is because the solvent molecules can solvate the linear portions of the rubber, but are constrained by the sulfur cross-links from totally dissolving the polymer. Another aspect of cross-linking is that the molecular weight increases enormously, which explains why solvent resistance increases and certain physical properties such as hardness, scratch resistance, and toughness are enhanced. The thermoset polymer is a three-dimensional network polymer. Cure must not be confused with dry time such as that measured in oil-containing polymers which dry by interaction with atmospheric oxygen. Here such terms as *set-to-touch, print free, time to lint free,* and *time for sand pickup* relate to the speed at which solvent evaporates and not to the ultimate cure or cross-linking of a coating system. Cure, therefore, refers to the cross-linking of a polymer to produce a three-dimensional network.

[1]Senior Consultant, Consolidated Research, Inc., 16731 Brick Rd., Granger, IN 46530.

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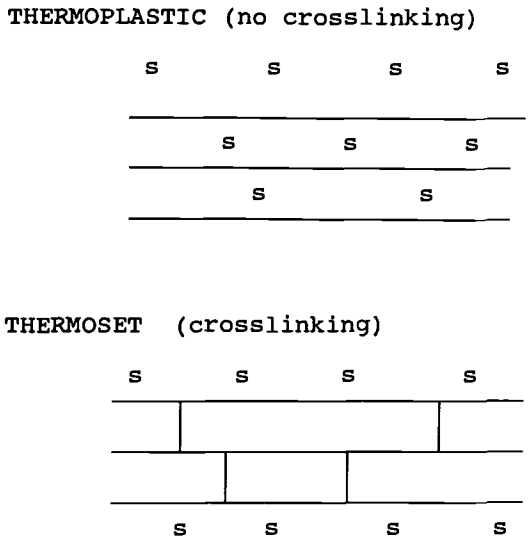


FIG. 1–Polymers.

TYPES OF FILMS

As described above, polymers can be classified as *thermoplastic* and *thermoset* in nature when derived from addition and condensation polymerization as well as by their physical response to heat and solvent action.

Thermoplastic

A long-chain polymer such as polyethylene is considered thermoplastic since it can be dissolved in certain solvents and can be repeatedly softened or melted when heated and hardened when cooled.

Thermoset

On the other hand, a polymer prepared, for example, from a phenol-formaldehyde condensate cannot be liquified and solidified repeatedly after it is formed. These polymers are termed *thermosetting* and tend to degrade if heated repeatedly. The reason for this is that they are cross-linked.

CURE MECHANISMS

Coating films can be made by a number of methods. The principal mechanisms of film formation are represented by lacquers, emulsions, and thermosetting (via oxidative cross-linking or by reactive cross-linking) coatings. For a review of film formation, the reader is referred to the Federation of Societies for Coatings Technology Monograph on Film Formation [5].

Lacquers

Lacquers consist of a thermoplastic polymer which is dissolved in a solvent. When the coating is applied, the solvent evaporates and a thermoplastic film is formed. This is the type of coating used in certain furniture and automotive finishes.

Emulsions

Another means for forming a thermoplastic film is film formation from an emulsion. In this case, a polymer, such as a vinyl acetate-acrylic copolymer emulsion (or latex), is cast onto a substrate and then the water carrier leaves the film by evaporation. In the latex, water is not a solvent but a dispersing medium. Microscopically, the polymer molecules look like tiny ball bearings suspended in water (Fig. 2). Surface active agents keep the polymer from settling. As the water evaporates, hydrodynamic pressure causes the small spheres to crowd closer and closer together until capillary action forces the particles to fuse and form a continuous film. If the polymer is too hard, a poorly adherent film forms. This is why paint manufacturers recommend that water-based, latex-type paints not be applied at low temperatures. At low temperatures, the particles cannot fuse properly, and the paint will fail prematurely. To facilitate fusion, small amounts of coalescing solvent such as diethylene glycol monobutyl ether (butyl Carbitol™ Union Carbide Corp.) are added. These solvents lower the glass transition temperature of the copolymer and facilitates fusion. These are examples of physical drying as compared to chemical drying discussed next (see Fig. 2).

Oxidative Cross-Linking

In oxidative cross-linking, a polymer is prepared from an unsaturated fatty acid or oil such as castor, tall, soya, linseed, or tung oil, and a small amount of a siccative (drier) such as

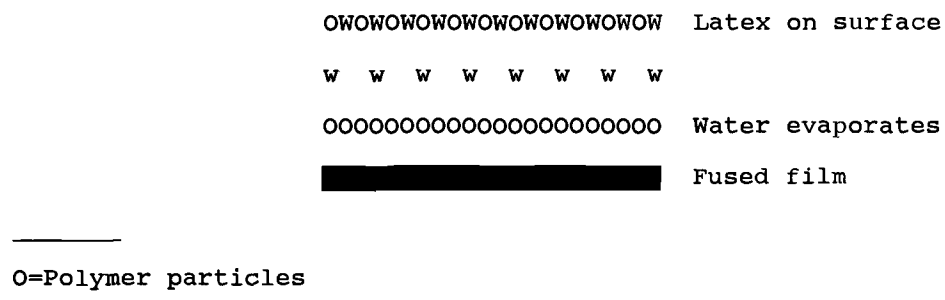


FIG. 2–Drying of a latex film.

lead, cobalt, manganese, or zirconium salts, for example, naphthenates, octoates, etc., is added. The film is cast by brushing, spraying, or other means and allowed to dry. In the first stages, the solvent evaporates, leaving a tacky film. The film can be easily deformed or thumb printed. But, as the film ages, it slowly becomes less tacky and finally print free and cured. What has happened? The film slowly absorbed oxygen from the atmosphere and formed hydroperoxides on the carbon alpha to the double bond. The drier decomposed the hydroperoxide and formed free radicals that initiated cross-links between the chains derived from the fatty acid portion of the alkyd (which imparts improved properties to the film), resulting in a cured or cross-linked film. A simplified reaction scheme is shown in the following [6]:

$$R{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}R' \xrightarrow{O_2}$$

$$R{-}\underset{\underset{OOH}{|}}{CH}{-}CH{=}CH{-}CH{=}CH{-}R'$$

$$R{-}\underset{\cdot}{C}H{-}CH{=}CH{-}CH{=}CH{-}R' + \cdot OOH$$

where R is $CH_3(CH_2)_4$ and R′ is $(CH_2)_7CO_2CH_3$.

The initial products are converted to polymers according to:

Initiation:	$RH + O_2 \longrightarrow R\cdot + \cdot OOH$
Propagation	$R\cdot + O_2 \longrightarrow ROO\cdot$
	$ROO\cdot + RH \longrightarrow ROOH + R\cdot$
Termination	$ROO\cdot + R\cdot \longrightarrow ROOR$
	$ROO\cdot + ROO\cdot \longrightarrow ROOR + O_2$
	$R\cdot + R\cdot \longrightarrow R{-}R$

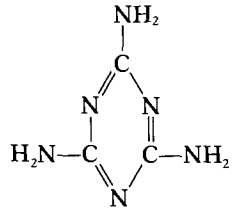
Termination by coupling doubles the size of the molecule since two fragments are now joined (assuming that the chain length is about equal). In this way oil-bearing oxidative curing leads to networks having the proper chemical and physical properties.

Reactive Cross-linking

In this type of cross-linking, a reactive intermediate is added to a polymer and a further chemical reaction is initiated either by heating alone, heating in the presence of a catalyst, or by some other form of initiation.

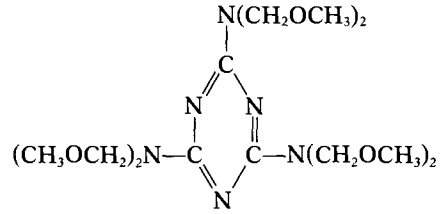
Melamine

Melamine formaldehyde condensates are used to cure a reactive polymer. Melamine is 1,3,5 triamino-s-triazine and is produced from the condensation of 3 moles of dicyandiamide:



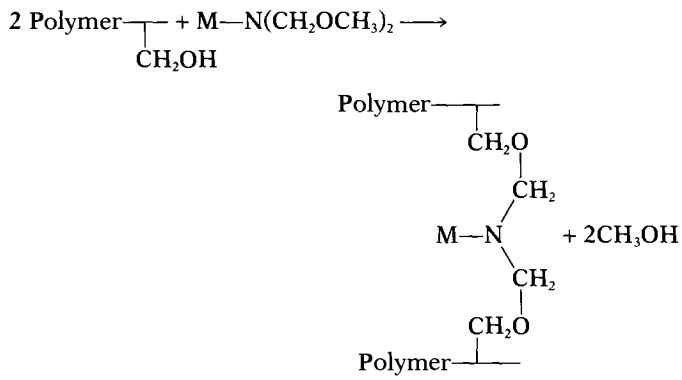
Melamine

Melamine can be condensed with up to 6 mol of formaldehyde and 6 mol of methanol to form hexamethoxymethyl melamine (HMMM). The reaction product has the following structure and is often referred to as MF resin:



Hexamethoxymethyl melamine

Hexamethoxymethyl melamine can be reacted to contain from one to six methoxymethyl groups. Methanol is used to cap the hydroxyl group to prevent premature reaction. Other alcohols are commonly used, including butanol and isobutanol. In applying a melamine formaldehyde resin, the resin usually is reacted with a functional polymer such as a thermosetting acrylic or alkyd polymer containing an acid or hydroxyl group that can react with the MF resin. This can be depicted in the following manner:



where M denotes a methoxy-substituted melamine functional unit. In this illustration, only two of the melamine methoxymethyl functions are shown reacting with the hydroxyl groups of an alkyd or other hydroxyl functional polymer. Note also the formation of a byproduct, methanol. Formaldehyde can also form as a byproduct.

Urea

A scheme similar to that described above for melamine is also applicable to urea formaldehyde (UF) resins. In this case, urea is reacted with formaldehyde and endcapped with either methyl, butyl, or isopropyl alcohols. A fully reacted urea intermediate would have a structure

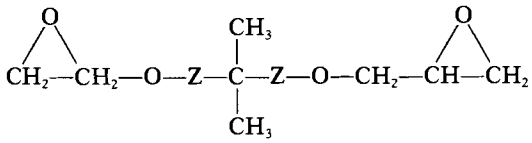
$$(CH_3OCH_2)_2{-}N{-}\underset{\underset{O}{\|}}{C}{-}N{-}(CH_2OCH_3)_2$$

N,N′ bishydroxymethylurea

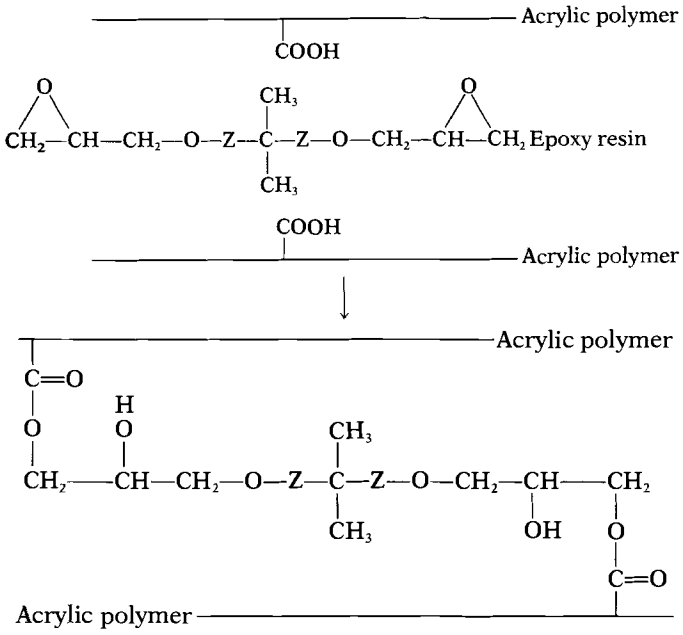
and is capable of reacting with hydroxyl groups to produce a cross-link with the elimination of byproducts as water, alcohol, and formaldehyde.

Epoxy

Epoxy resins are derivatives of cyclic ethers. Aromatic epoxy resins are produced from the reaction of epichlorohydrin and bisphenol A, and the latter is a condensation product of acetone and phenol. Aliphatic epoxy resins are prepared by the peroxidation of unsaturated linear or cyclic olefins. A simple epoxy, the diglycidyl ether of bisphenol A, is shown below (Z = phenylene group)



These epoxy functional groups can react with active hydrogen groups such as amines, hydroxyls, and acids. For example, they can react with acid groups in a thermosetting acrylic, alkyd, or other polymer and produce a cross-linked polymer. It is interesting to note that the reaction product of the epoxy and acid function produce additional hydroxyl groups which can be reacted with a melamine formaldehyde or urea formaldehyde adduct to produce improved properties, such as hardness, chemical resistance, or solvent resistance in the cured films. The reaction of two acrylic polymer chains with an epoxy resin is shown as follows:

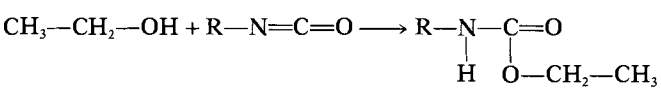


where Z represents a phenylene group.

Cross-linked acrylic polymer

Isocyanates

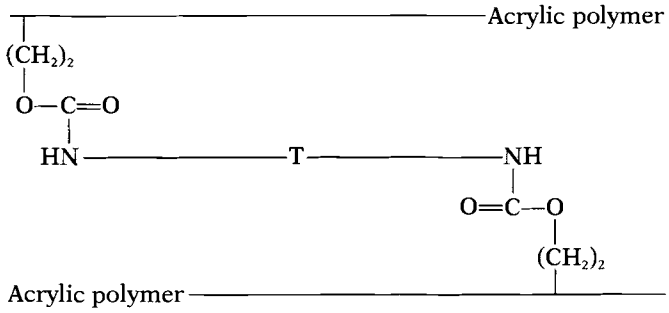
The term urethane applies to the reaction product of an hydroxyl group and an isocyanate. For example, an alcohol and isocyanate react by rearrangement to produce a urethane



Alcohol + Isocyanate Urethane

This reaction is used in applying isocyanates to the production of insulation and seating foams, reaction injection moldings, and high-performance coatings such as for aircraft. In this case the isocyanate is a di- or triisocyanate, which leads to cross-linking. Toluene diisocyanate is widely used, but other isocyanates such as 1,4-diphenyl methane diisocyanate, isophorone diisocyanate, and trimers of hexamethylene diisocyanate are also used. The higher-molecular-weight isocyanates are preferred for their lower vapor pressure, thus providing for improved working conditions.

Isocyanates are used to cross-link a variety of polymers containing hydroxyl or amine functionality. In the case of amine functionality, a urea cross-link is formed. For example, an acrylic polymer can be prepared from methylmethacrylate, butyl acrylate, and hydroxyethyl methacrylate. This polymer can be cross-linked through the pendant hydroxyl groups of the hydroxyethyl methacrylate portion by polyfunctional isocyanates:



Urethane cross-linked acrylic

T = $CH_3—C_6H_3—$ (from toluene diisocyanate)

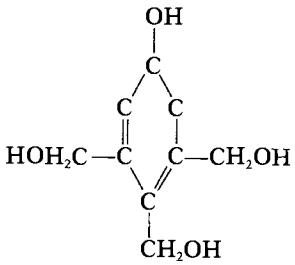
Urethane cross-linking is also used in polyesters where the hydroxyl groups are obtained from polyfunctional alcohols, such as trimethylolpropane or pentaerythritol. Similarly, epoxy resins can be cross-linked through the hydroxyl groups formed during epoxy reactions.

Catalyzed Cross-linking

This type of cross-linking is used in phenolic and silicone reactions wherein a catalyst is added to facilitate the cross-linking reaction.

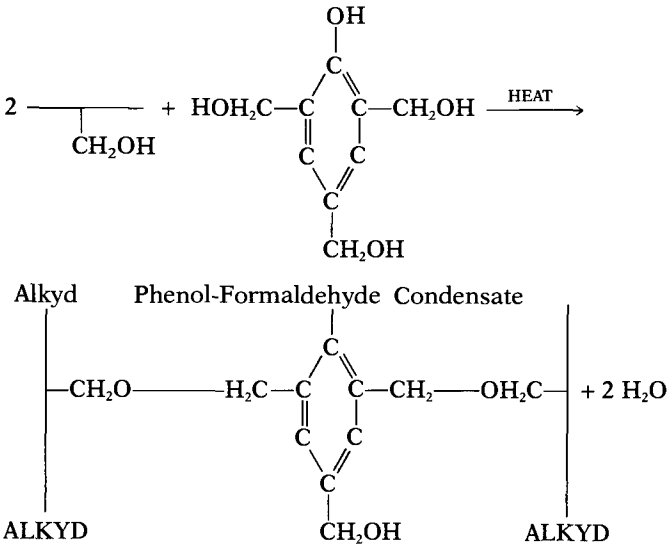
Phenolics

Phenolic resins are condensation reaction products of phenol or substituted phenols and formaldehyde. Two types of phenolics are obtained depending upon the catalyst and reaction conditions. Using an acid in its preparation, a thermoplastic, soluble novolac resin is obtained. Under basic conditions, the thermoset product formed is a resole resin which is cross-linked at the final stages of the reaction. A phenol-formaldehyde condensate may have a structure as shown:



Phenol-formaldehyde (P—F) condensate

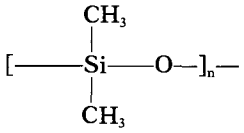
Alkyd resins can be cross-linked by reaction of the hydroxymethyl function and an hydroxyl group on the alkyd with the elimination of water:



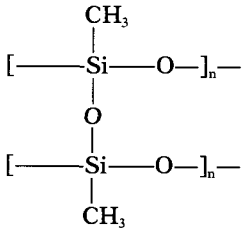
Cross-linked alkyd

Silicones

These useful polymers are prepared from silicon by chlorination, then subsequent reaction with alkyl or aryl halides to form alkyl/aryl chlorosilanes. Upon hydrolysis, these produce silicones. The alkyl silicones, such as dimethyl silicone,



are low-molecular-weight or cyclic materials used in antifoam applications. The linear forms are specialty elastomers. Blends of methyl and phenyl silicones have higher-temperature resistance and find use in heat-resistant coatings or polymers. Silicones can be cross-linked when prepared with multifunctional silane monomers such as trichloromethyl silane. Upon hydrolysis, the silicone chains can be cross-linked through siloxane bridges:



Cross-linked silicone

Silicones can also be cross-linked by peroxide initiators. In this case a silicone monomer containing a vinyl or allyl group is copolymerized to provide an active site along the chain. When used in a gasket or caulk, a small amount of a peroxide is added which initiates polymerization and cross-links the resin system. Silicone reactions are usually catalyzed by organo zinc or tin compounds.

Curing can also be accomplished using radiation as a source for initiation. Electron beam (EB) and ultraviolet radiation is used to cure coating films. These processes induce either free radical or carbonium ions to initiate polymerization, which occurs rapidly at ambient conditions.

CURE MEASUREMENT

It is very important for the user of coatings to know whether a coating is adequately cured. This can be done quickly in qualitative testing or in more sophisticated test methods requiring instrumentation. The rapid methods are desirable because of time and cost, but in some cases do not really tell the true story. In some cases, even instrumented testing only tests a certain range of cross-linking and could lead to erroneous conclusions. We shall discuss the qualitative methods first, then proceed to the more quantitative. What should be borne in mind is that we are attempting to ascertain a molecular process, cross-linking, and its relationship to coating performance.

Many thermoplastic coatings "dry" by simple evaporation of solvent, and though cure was defined above as the cross-linking of a polymeric system, such drying of lacquers can be considered a form of curing even though no cross-linking occurs. This is true for nitrocellulose lacquers, cellulose acetate, and solvent soluble acrylics where no cross-linking takes place. To measure cure for such coating, the time for either print-free or tack-free is measured. At some time during evaporation, the coating goes from tacky, to set-to-touch, to tack-free. Upon further drying, the coating becomes print-free, whereby a thumb print will not be visible on the coating. This can also be measured by dropping cotton linters onto the surface and noting the time after which they do not adhere to the coating. Also see ASTM D 2091, which describes a standard method for print resistance of lacquers.

These tests also apply to coatings which dry by oxidative cross-linking, for example, alkyds. Here, times are noted for solvent evaporation, and the coating is monitored for set-to-touch, then print-free.

Solvent Rubs (ASTM D 4752 Test Method for Measuring MEK Resistance of Ethyl Silicate (Inorganic) Zinc-Rich Primers by Solvent Rub)

A convenient, often-used method for determining cross-linking involves solvent rubs. A cloth soaked with methyl ethyl ketone (MEK) is rubbed vigorously on the film, and then the film is examined after a specific number of rubs. Acetone is also used for this test. If the film is removed, softened, or loses gloss, then the film is considered not adequately cross-linked. Films which are unaffected are considered cured. For example, certain acrylic, epoxy, or polyester coatings can survive this test. The problem with this test is that the individual testing the coating is not standardized. One person may exert much more pressure than another, and this can affect the final result.

Hardness Measurements

Another way of obtaining information concerning cross-linking is to measure some physical property such as, hard-

ness, scratch resistance, or impact resistance. There are a number of tests which provide this information.

Knoop and Pfund Hardness (ASTM D 1474 Test Methods for Indentation Hardness or Organic Coatings)

A useful test of cure is to measure the Knoop hardness in which a pyramidal diamond indenter is pressed into the film to cause indentation. The method is described in ASTM D 1474. A weight is applied to the indenter for a specific time, and the length of the indentation line is measured with a microscope. The Knoop hardness number (KHN) is calculated from [8]:

$$\text{KHN} = L/A_p = L/l^2C_p$$

where L = applied load (kg), A_p = projected indentation area (mm^2), l = length in mm of the long diagonal of the indentation mark, and C_p is an instrument constant. Because of the thinness of coating films, this method is more useful in plastics since it requires almost a 75% indentation into the film and can be influenced by substrate considerations.

The Pfund Hardness Number (PHN) is obtained using a hemispherical quartz or sapphire indenter, which is pressed into the film. The Pfund Hardness Number is calculated from:

$$\text{PFN} = L/A = 4L/\pi d^2 = 1.27\,L/d^2$$

where

L = applied load in kilograms,
A = area of projected indentation in mm^2, and
d = diameter of the projected indentation in mm.

Sward (See ASTM D 2134, Sward Rocker, and ASTM D 4366, Pendulum Damping)

Sward hardness depends upon the change in surface properties and viscoelastic properties of a film. This method, which was discontinued in 1990, is used for automotive finishes and consists of a rocker containing two spirit bubble indicators. The pendulum is rocked, and the number of swings are recorded and a reading taken at the point where the swings are equal to half the original value. Several types of pendulum units are used including Sward, Perzoz, and Koenig. As cure increases, the Sward number increases. The value of a Sward test is that a number is obtained which can be compared to other coatings. This test must also be conducted under very clean conditions, as lint and surface imperfections can interfere. Temperature control is important in this test as in other tests involving determining physical properties of coatings. The problem with this test is that it only measures cross-linking density to a point; then cannot detect over cure since a plot of Sward numbers versus cure tends to reach a limiting value. A comparison of values obtained by different test methods is shown in Table 1 [9]. Note how the values differ, especially between different brands of pencils and the limiting value of Sward Hardness.

Pencil (ASTM D 3363 Test Method for Film Hardness by Pencil Test)

Pencil hardness is a test which was developed by the manufacturers of pencils who tried to develop a means for checking the quality of pencils. Someone suggested scratching a paint film, and it was noticed that the different hardnesses of pencils were able to penetrate through the coating. This test was later used by coating technologists, and it is widely used in the industry today. In this technique a number of pencils with known hardnesses are employed. The pencil is trimmed so that 5 mm of lead is exposed. The lead diameter is 1.8 mm and is sharpened by rubbing it perpendicular to the surface of No. 400 carbide abrasive paper. The pencil is held at a 45° angle to the coating and pushed along the surface to peel away the coating. The pencil which fails to scratch the coating is the value used as pencil hardness. This method is simple, the equipment low in cost, and the results can be quickly obtained. However, values can differ depending upon the operator, the method of sharpening the lead, and the variances of lead hardness from different pencil lots and manufacturers.

Gardner Impact (ASTM D 2794 Test Method for Resistance of Organic Coatings to the Effects of Rapid Deformation (Impact))

This is a valuable test which measures the impact resistance of a coating and can be used to correlate with cure. An undercured coating may exhibit a lower Gardner Impact value, but as cross-linking density increases, the impact values improve. The test consists of placing a coated flat panel under a weighted spherical ball assembly and then dropping the weighted ball onto the panel from different heights. The cylinder in which the ball assembly is mounted is calibrated such that an operator can measure the impact directly in inch pounds. Impact measurements are done by dropping the ball directly on the coating surface or on the reverse side. The results are reported as inch-pounds direct or reverse. Direct impact is less severe than reverse impact. A dimple is formed in the test panel which can be examined visually or with a X10 glass to determine the extent of cracking which occurs. An appliance acrylic may have a direct impact of only 10 in.-lb, while a polyester urethane powder coating may have a reverse impact of 160 in.-lb. The value of the Gardner Impact test is that the test can be done quickly, it is widely recognized in the coatings industry, and it gives some correlation with cross-link density in that the optimum physical properties of a coating develop as the molecular weight increases.

Thermal Analysis

Thermal analysis is an important analytical tool for determining the response of material to changes in temperatures. This method of analysis can be used to monitor the glass transition temperature, T_g, of a coating, and this can be related to the cross-linking density. For example, a ladder of paint panels cured at various times or temperatures can be prepared and then studied by thermal analysis to determine the change in T_g as a function of bake schedule. From this, the optimum cure cycle can be determined to insure a quality finish.

Thermal analysis units have several modes for determining T_g: differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and dynamic mechanical analysis (DMA) are useful tools for obtaining quantitative mea-

TABLE 1—Hardness test correlation.

			Pencil (Brands)				
Panel No.	KHN	Sward	A	B	C	D	E
1	3.09	24	5B	6B	5B	6B	4B
2	4.33	28	4B	6B	6B	6B	4B
3	2.77	24	5B	6B	5B	4B	3B
4	2.61	22	3B	4B	5B	4B	3B
5	5.81	38	2B	2B	2B	2B	HB
10	25.7	54	H	H	H	H	2H
12	39.1	40	3H	2H	2H	4H	3H
14	...	40	8H	9H	7H	7H	9H

sures of cross-linking by measuring T_g. The glass transition temperature is a second order transition that represents a temperature where segmental motion occurs along a polymer chain backbone, and it is accompanied by a volume change. A comparative study of changes of cross-linking measured by Sward hardness, evaporative rate analysis, and DSC showed that T_g changes can be followed to high levels of cross-linking, whereas Sward measurements reached a limiting value while T_g continued to rise [*10*].

With DSC, a plot of endotherm/exotherm is made as a function of temperature at a set rate of temperature rise. As the T_g is reached, there is an abrupt change in the endotherm which appears on a plot. Similarly, T_g can be measured using a plot of change in expansion with temperature with the TMA mode. Here a sample is placed under a quartz probe and then heated. As the film expands a plot is obtained in which a change in slope occurs. The intersection of the tangents of the expansion curve yields the T_g value. In the penetration mode a depression occurs indicating the T_g. Plots can be made of T_g versus bake cycle to note the optimum T_g of a coating. Further details on thermal analysis applications can be found in the literature [*11–13*].

Dynamic Mechanical Analysis

Another way of obtaining T_g is to use dynamic mechanical analysis in which a coating film is fixed to the ends of a tuning fork and the fork driven over a frequency range and at different temperatures or at a fixed frequency with varying temperature to provide a plot of damping versus temperature. This information yields T_g as well as mechanical damping information about the film [*14*].

Torsion Pendulum [*14,15*]

Another method for measuring dynamic mechanical properties of coatings is to suspend the film with a weight, then twist the weight so that it will oscillate as a pendulum. This is not entirely acceptable since coating films may not have the strength to support the weight of the apparatus. One way to overcome this is to invert the apparatus so that the pendulum weight is suspended with counterweights. A more practical method is to use the torsion braid pendulum in which a fiberglass braid is saturated with a coating and the pendulum oscillated. As the coating cures, changes in oscillation can be correlated with damping and T_g.

Impedance Measurements

Myers [*16*] studied the drying behavior of latex systems using ultrasonic impedance measurements. In this work, a latex coating was cast on a quartz crystal and ultrasonic energy was beamed at an 11° angle at the underside of the coating and reflected to a detector which measured the attenuation of the initial beam as absorbed by the drying coatings. As water evaporated, there were changes in impedance that could be correlated to drying.

Evaporative Rate Analysis

A novel method for studying cure is evaporative rate analysis (ERA) developed by John Anderson [*17*]. This work was carried out to determine the cleanliness of the surface of spacecraft. Anderson reasoned that if a radioactive C^{14} liquid would be placed on a clean surface, the evaporation rate would be retarded due to cleanliness. In fact, however, the opposite was true.

Nevertheless, this method was developed to measure degree of cleanliness. If a small amount of diethyl succinate-C-^{14} is deposited on a surface and a controlled sweep of nitrogen is applied, the rate of evaporation can be monitored using a Geiger counter. The principle is that on a clean surface there is no interaction between the solvent and the clean substrate, and normal evaporation occurs. If, however, the surface contains a contaminant, then the radioactive liquid will interact with the surface contaminant and retard the rate of evaporation of the radiocarbon. Plots can be obtained relating cleanliness to evaporation rate.

Anderson applied this technique to the cure of organic coatings. He showed that in an undercured surface solvent retention increased, leading to longer residence of the radiocarbon on an undercured surface. This is understandable in view of the example given in the beginning of this chapter of the ability of a solvent to pass through a wire fence analogy. By preparing coated panels having different cure times or temperatures, then measuring the ERA of each panel, a plot of retention versus bake is obtained. This method was applied to the measurement of cure of a variety of coatings by many coatings technologists [*10,18*]. The only problem was that there was no quantitative means for measuring the relationship of ERA to cure until it was shown that DSC of T_g

could be correlated to the values obtained using ERA measurements [*10*].

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37

Film Preparation for Coating Tests

by Robert D. Athey, Jr.[1]

THE PERFORMANCE OF A COATING FILM in a test is likely to be dependent on the physical form of the film. For instance, film thickness is an important factor in physical and appearance measurements (until the coating gets too thick), so there must be some control of the film thickness. Appearance is also related to how smooth the film surface is, and care to make the film appropriately will ensure that the appearance measurements are germane to the end-use. The substrate used as the carrier for the test film, even temporarily, may affect the property measurements, as well.

The primary concern in making films for tests is that the film prepared be homogeneous and consistent with previous or future films for the same test. The jargon of the trade calls the art of making films "casting," but many film formation methods are used to form the film, and each method has its own set of advantages and drawbacks.

TEST REQUIREMENTS OF FILMS

Test requirements come in two classes, appearance and physical properties. Choice of application method for the film may affect the appearance in some cases. For instance, the "multicolor" paints must be applied by dip or spray techniques for laboratory testing, or the appearance does not give the desired mottle of nearly circular spots. Roller, brush, or even drawdown bar will cause these spots to become streaks. Choice of application method for appearance includes drying technique, as some films require special drying conditions to attain their desired special appearance. Examples include leafing aluminum flake "metallic" look paints, hammertones, and wrinkle finishes.

Choice of application method driven by physical property testing is also necessary. Think carefully of the three kinds of stresses (tensile, compression, shear) and recognize that all are blended in a hardness or adhesion evaluation by indenter, pencil, mandrel bend, or dart impact test on a coating. Recognizing these stress combinations can make one aware of film preparation needs. In cases where adhesion is stronger than cohesion of the film, one should be able to distinguish between adhesive failure and cohesive failure. Film preparation should not conflict with these objectives.

The physical properties to be tested in specific ASTM methods have a "significance and use" section in the method to ascribe the relation of the test value to some "in use" performance criterion. The preparation of the test film should thus correspond to the standard field application of the material, as well.

Another portion of film influence on the test is film thickness. The presentation by the Technical Committee from Toronto in the 1990 National FSCT meeting and Paint Show [*1*] dealt with hardness measurements in films of varying thickness. However, the control of film thickness was not as straightforward as might have been thought. Hardness values turned out to be dependent on film thickness along with other equally important variables [*2*].

Fluid rheology, concentration, and other factors govern the amount of coating left after the application process. Knowing the process variables associated with a film-casting technique are essential to getting what is needed for the ultimate test and results therefrom. Certain other properties of the film (opacity, permeability, erosion rate by some attacking mode, etc.) will depend on the thickness of the film. So, understanding thickness control in the casting process is crucial to obtaining meaningful results in terms of meeting specifications in reproducibility.

In instances where fluid or gas permeation resistance or corrosion barrier properties are to be tested, a "pinhole," "holiday," or "mudcrack" in the film is a fatal flaw. The film preparation technique must eliminate (as much as possible) any such fatal flaw, or the test method should prescribe what is to be done (for example, replications) in cases where an unseen fatal flaw is detected by the test.

FILM CASTING TECHNIQUES

Free Films

Free films, that is, films not applied permanently to a substrate, are used for a wide variety of tests and accordingly vary in thickness and size. The most common castings of free films are used for permeation or strength and elongation testing. They can also be used for cold flex tests or moisture/solvent absorption studies related to permeation. Free film thickness can be measured as described in ASTM D 1005: Test Method for Measurement of Dry-Film Thickness of Organic Coatings Using Micrometers.

Probably the most common free film castings are laid down on a "nonstick" surface, such as the silicone-coated papers (available through Leneta and other suppliers) or TEFLON™ or polyethylene sheets. Release substrates are described in ASTM D 823: Test Methods for Producing Films of Uniform

[1]Athey Technologies, P.O. Drawer 7, El Cerrito, CA 94530-0007.

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Thickness of Paint, Varnish, and Related Products on Test Panels. Lack of release-substrate wetting is the most common problem encountered when trying to obtain a continuous film. Water-borne coatings are especially difficult to formulate for good wetting of these substrates. One trick to use with such formulations is to prepare the sample at higher than normal solids content, which results in increased viscosity, and resistance to beading is improved. An alternative is to apply several coats until the dried "beaded-up" portions merge to form a continuous film.

A vacuum plate makes it easier to hold down the paper or polymer film for film casting and is an aid to good results. Figure 1 is a diagram of the vacuum plate formed from aluminum. Older versions had eyes at the bottom surface through which screws could affix the plate to a table top. If this system is to be vacuum supplied from a sink faucet aspirator, a liquid trap (vacuum side-fitted Erlenmeyer flask) should be placed in line between the vacuum plate and the aspirator. This will ensure that any liquid coming from the aspirator will not get to the vacuum plate or coating substrate.

Grenko [*3*] suggested several coated paper techniques for obtaining free films, such as decal paper coated on the face side or outdated matte or semimatte photopaper. The decal paper could be floated on water and the paper peeled off. Grenko did not describe the removal of photopapers from the film. He also cited Sager [*4*] for a technique using an embroidery hoop for holding a nonmoisture proof cellophane. After the coating film had been applied, one simply poured water on the inverted cellophane and the coating film dropped off. These techniques are likely to be most appropriate for solvent borne or 100% reactive formulations. Water-borne coatings may be inappropriately leached or weakened by the water used to loosen and isolate the films.

Grenko [*3*] also mentioned the use of metal substrates for free film isolation. Brightwell [*5*] used glass onto which a thin silver film had been vacuum deposited. Bayor and Kempf [*6*] used thin aluminum foil that was later dissolved from most of the back with hydrochloric acid doped with a minute amount of platinum chloride. The latter dissolved off only enough aluminum foil to leave a foil "frame" at the edges of the film to support it and to facilitate handling. This technique with aluminum foil dissolution in an acidic, aqueous medium presumes no sensitivity of the coating components to acid or water.

For thicker films (1 cm or more), a PYREX™ or TEFLON™ coated baking pan can be used with some success. For instance, about 300 mL of a latex formulation in a 9 by 12 in. (23 to 30 cm) Pyrex™ baking dish will yield plenty of thick film for testing. Occasionally, there is a "mudcracking" problem, but it can be reduced periodically by releasing the edges of the film from the vertical sides of the dish with a spatula to allow uninhibited shrinkage. This way usually results in increased size pieces, and 1 in.^{2} (6.25 cm^2) is all you need for the moisture absorption or solvent swell test. Using this technique, it is possible to obtain large enough pieces for moisture vapor transmission tests at application thicknesses that are common for roof coatings.

The "mudcracking" problem is serious for any coating. The cause is the lack of "wet gel strength" to resist the tensile stresses within the shrinking membrane. Strictly speaking, unless the coating cross-links, it is not a gel, but simply a high-viscosity fluid or "pseudogel." The problem may be alleviated by assuring that the upper surface does not "skin over" through controlling the humidity or solvent-vapor environment over the drying surface.

The literature describes mercury pool casting [*7,8*] or tin foil casting [*9*] with mercury amalgamation used to remove the tin without stressing the coating film. ASTM D 4708 Practice for Preparation of Free Films of Organic Coatings also describes the tin foil amalgamation technique. These techniques are no longer in common use, as the mercury vapor is deemed a health hazard.

Rarely, but occasionally, a free film of a polymer or binder material is needed for testing water vapor permeation or absorption, for instance. Some of these tend to be tacky, and powder applied to the surface will make them easier to handle. Although pearl cornstarch is preferred over the powdered talcs, baby powders and similar talcum powders are often used.

Rotational casting is a means of obtaining nonporous, nonmudcracked free films. The standard jar-mill roller (see Fig. 2) may be used with a variety of open containers (quart or gallon jars, earless paint cans with a 4-in. (10-cm) circle cut out of the bottom, . . .) to centrifugally cast the film with good thickness control. An alternative device, the Caframo REAX 2

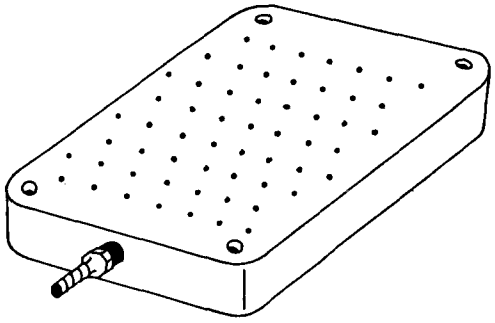

FIG. 1–*Vacuum plate*—pulling a vacuum through the side nozzle holds paper or paperboard substrates tight for drawdown film casting. (Courtesy P. N. Gardner Co.)

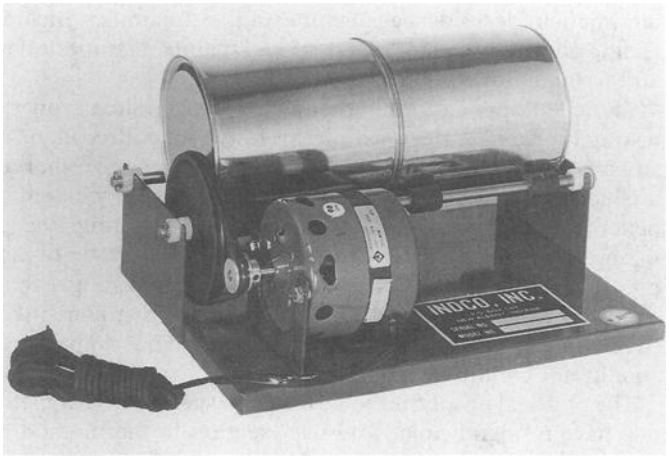

FIG. 2–*Lab roller mill*—Although this device is most often used for pebble milling, an empty earless paint can on the rollers may be used to cast films. (Courtesy of Indco Inc.)

rotating mixer [*10*], may be used to hold the paint can with its main axis along the rotation axis of the clamp (see Fig. 3).

This rotational casting technique was used successfully in a study by the Los Angeles Society for Coating Technology Technical Committee to obtain tensile and moisture vapor permeation film samples from acrylic latex compounded with silane modified talcs [*11*]. It is derived from an older practice at the Thiokol Rubber Co. to form films of castable elastomers in a rolling pipe [*12*].

Equipment for this technique is easy to set up and use. Introduce 100 mL of coating into a 1-gal can and let it roll overnight. This will result in a film approximately 6 by 18 in. (15 by 46 cm). That is a sufficient amount for 6-in. (15-cm) tensile bars and 2-in. (5-cm) permeation circles. Close control of film thickness is achieved by knowing the area of the cylinder and concentration. From these, the weight of coating needed can be calculated. Films of tacky coatings or pressure-sensitive adhesive formulations can be made by this technique. After the film is formed, the can is placed in a refrigerator or freezer to facilitate film removal.

To obtain a centrifugally cast powder coating film, a sample of the powder is introduced into the can. Then, a hot air gun is held at the outside of the rolling can, and the powder coating will melt to coat the inside. Care is needed to eliminate scorching, and practice is needed to determine how close the flame should be to the can to get a good film. Other techniques to obtain a film include melting on a Teflon™ sheet on a hot plate or in between Teflon sheets in a heated (Carver, PHI, . . .) press.

Spraying is occasionally used to make free films (e.g., onto a silicone-coated paper). There is no problem with this technique when it is done by a skilled practitioner. However, films made with this technique may not give as good permeation test results as from one made by a film from a fluid-flow technique.

A note of caution should be added about handling free films made for physical testing. Any undue stresses may chip or crack the film. This is especially important for permeation or physical property tests. In the case of the latter, some materials are "notch sensitive," that is, the results of a tensile or other physical test may be reduced by the presence of a notch, scratch, or crack in the film [*13*].

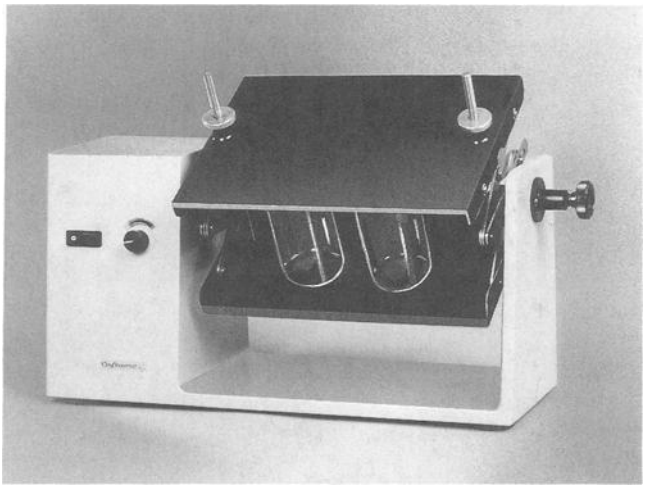

FIG. 3–*Caframo "REAX 2"*—This device was designed as a rotational mixer for fluids, but a gallon paint can will fit in it for rotational film casting, as well. (Courtesy of Caframo Ltd.)

Dry Coatings on Substrates

Test coatings on a substrate are generally applied for a wide variety of appearance and physical property tests. Color and opacity are commonly evaluated on coated paper charts, though unsealed paper charts with a porous surface are available, as well. Coating on substrates to simulate actual use is common so the paint lab has many kinds of steel, aluminum, wood, or other substrates in stock as needed by the customer or the paint company.

Plastic panels are rarer, but can be made available when needed. Several companies now offer such products. Plastic panels may need special surface preparation techniques to assure wetting and adhesion (solvent washes, chemical etchs with alkali or acid, low-temperature plasma, or corona discharge or chemical oxidation, etc.). As painting plastics become more and more important for automotive, computer, sign, and other industries, the manufacturers will make panels available to potential paint suppliers.

Panels of metal are a special case for the preparation of test films for paint. One may have to do a precoating surface preparation on the metal, and consultation with appropriate specifying agencies may be necessary. The Steel Structures Painting Council has many grades of hot-rolled steel preparation techniques that vary from wire brushing through sand blasting to expose "white metal" [*14*]. Other preparations such as phosphatizing, galvanizing, anodizing, etc., are unique to specific industries or industry segments and will require lab preparation of panels or freshly treated panels from the customer or a commercial source. An annual handbook contains descriptions of some of these techniques for lab usage [*15*]. Preordered steel panels that are subsequently stored in special corrosion-inhibitor-treated packaging may skew exposure tests if they are not rigorously cleaned of corrosion inhibitor just prior to the coating steps. Cleaning procedures may require rinsing with hydrocarbon solvent or acetone and hot-air drying just before paints are applied. Exposure panels made of metal must also have special edge protection to ensure that only the coated face has the exposure test applied.

The casting technique on a paper or paperboard substrate is a skill one learns through apprenticeship. First, the panel needs to be clean and dust free. For horizontal castings, which is a way to obtain good flat films, it is necessary to ensure that the surface is level during casting and drying. Tape the chart or panel to the level surface so it doesn't curl as the film loses solvent or dispersing media and tries to shrink. Unsealed paper charts will curl in a convex manner since any water in the coating swells the paper fibers, and the substrate may try to curl the sheet in a concave manner when the film tries to shrink across the top surface from which evaporation is taking place. Vacuum plates are available, as noted earlier, to hold down the paper, foil, or cardboard chart during the film-casting process. The paper board chart should be stored in the same humidity environment that will be used in drying/curing the coating as the wood-pulp fibers are hygroscopic.

Concrete, plaster, and asphalt/gravel test blocks or panels may be prepared in the lab or may be purchased. However, whenever possible such blocks should be obtained from the customer since paint-lab results may not compare well with the customer's results if details such as porosity, surface salinity, surface pH, soluble calcium or sodium ion content, etc., are not equivalent. These materials may be hygroscopic and will need equilibration in the drying/curing environment prior to coating. In addition, some concrete castings, that is, tilt-up wall constructions, often have surface residues of form coatings that had been used to aid release from the forms. Surface characterization for such release aids or rigorous cleaning may be needed. There is an ASTM standard practice for preparation of mortar panels for testing paints: ASTM Method of Making and Preparing Concrete and Masonry Panels for Testing Paint Finishes (D 1734).

Grenko [*3*] has described press coating of bitumens on aluminum or felts, with shims placed in the press to attain appropriate thickness. His work was based on earlier work by Greenfield [*16*].

Wet Films for Testing

There are a variety of reasons one may want to have a close look at the wet film. Simply watching the drying process may make any problems with moisture condensation on the film, pigment float, etc., apparent. There are test films made to assess wet hiding or sag resistance (ASTM D 4400: Test Methods for Sag Resistance of Paints Using a Multinotch Applicator). Good film casting practice, for example, a level surface for casting, consistent technique, etc., is a requirement for reproducibility of results. Equipment needed for special tests will be included in the following section.

EQUIPMENT FOR FILM PREPARATION

Drawdown Bars

The drawdown bars are the simplest of the film casting devices to use. One simply makes a puddle of coating on the desired substrate and moves the drawdown bar over the puddle to make the desired wet film thickness. Application of the film with a drawdown bar nominally gives a good continuous film, but the spacing between the bar and the substrate may have little to do with the film thickness obtained. Speed of pulling the drawdown bar over the fluid will affect the film thickness since fluid rheology influences film thickness. High-molecular-weight polymers may cause the edges of the film to draw in and increase the wet-film thickness. The formulation may not wet the drawdown bar, and this adds another factor to the control of film thickness. Wetz and coworkers [*17*] showed almost 100% deposition of the wet film and found a relationship between wet-film and dry-film thickness.

$$T_{df} = 0.057 + 0.588GS(\rho_l/\rho_f), \text{ or}$$

$$T_{df} = 0.057 + 0.955T_{wf}(\rho_l/\rho_f),$$

where:

T_{df} = dry film thickness, mils
T_{wf} = wet film thickness, mils
ρ_l = density of liquid
ρ_f = density of dry film
G = clearance of drawdown bar(mils), and
S = weight fraction of solids in liquid.

Grenko [*3*] makes the point that these relationships are only true for drawdown blades having substantial flat surface between the leading edge of the bar and the trailing edge. The Byk-Gardner information [*18*] suggests the following expectations for varying film thicknesses cast:

TABLE 1—Drawdown bars for film casting.

Type	Design Details	Supplier[a]	Reference
"Bird" knife	Permanent fixed gap	P. N. Gardner	[*3*]
Two-path applicator (Wasag [*11*])	Bar has two cuts of different depth machined into top and bottom	P. N. Gardner	[*20*]
Eight-path applicator	Stainless steel square tube with eight different depth cuts in each of top and bottom edges	P. N. Gardner	[*20*]
Gardner "Microm" applicator (also Hercules-Gardner adjustable [*3*])	Micrometers on each side lower or raise blade of "U" shaped deviced	P. N. Gardner	[*20*]
"Universal" blade applicator	Blade forms "U" shape with sides having slots and thumb screws to raise or lower	P. N. Gardner	[*20*]
Dow latex film applicator	"U" shaped blade with wider cut for larger gap so second cast film covers first	Byk-Gardner	[*3*]

[a]There may be many other suppliers, but only one is cited herein as a space savings technique.

15 to 100 μm	50%
100 to 300 μm	60%
300 to 500 μm	80%
over 500 μm	90%

The hand-held drawdown bars are covered in an ASTM specification: Method E in ASTM D 832, Practice for Rubber Conditioning for Low-Temperature Testing.

A wide variety of drawdown bars are commercially available, though your local machine shop can make special orders of any design, if needed. Table 1 lists a few of the available types of drawdown bars, with commercial sources reports on them. Some rectangular design devices have differing gap depths on the sides so one may choose the film thickness needed for casting (see Figs. 4 and 5).

Stainless steel or aluminum are the preferred materials of construction, as corrosion can damage the region of the drawbar controlling thickness of applied film. Good laboratory practice dictates immediate cleaning of the paint contact surfaces after every usage to minimize the threat of corrosion or other damage. A caution on marking the drawdown bars, as some manufacturers label them not with the gap spacing, but a number half the gap spacing since that is the expected wet film thickness to be obtained.

Some drawdown bars have film thickness adjustment choices by micrometers or other techniques (see Table 1 and Fig. 6). When these are used, the settings should be checked with feeler gages to make certain user wear has not made them inaccurate. These also require dismantling and cleaning after every use. If oil is used to inhibit corrosion and make the mechanics move smoothly, make sure they are rigorously cleaned of oil prior to usage.

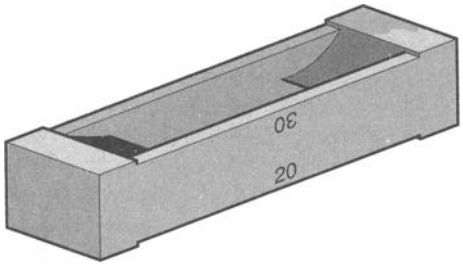

FIG. 4–*Applicator frame/step gap applicator*—Two film thickness choices are available with this device. (Courtesy of Byk-Gardner Inc.)

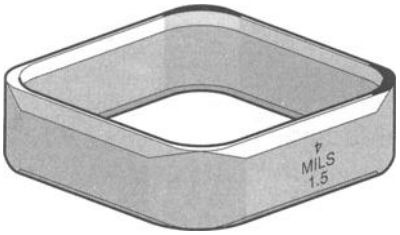

FIG. 5–*Multiple clearance applicator*—Eight film thickness choices are available on one device. (Courtesy of Byk-Gardner Inc.)

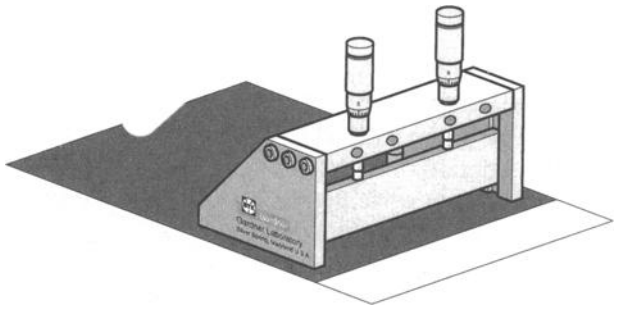

FIG. 6–*Film casting knife*—Micrometers adjust the blade clearance. (Courtesy of Byk-Gardner Inc.)

Several drawdown bars have gradations of cuts into the wet-film thickness controlling surfaces. For instance, the Erichsen suppliers offer the Kruse Multi Clearance applicator, having six to ten adjacent film strips of 10 to 200 μm in thickness for assessment of color yield, opacity, . . . (see Fig. 7) [*19*]. A similar device, the Leneta TG19 Logicator, is intended for hiding power and spreading rate measurements. It is available from P. N. Gardner [*20*] and has eight "gates" ranging from 2.65 to 10.4 mil in depth.

There are motorized film application devices specified in ASTM D 823, Test Methods for Producing Films of Uniform Thickness of Paint, Varnish, and Related Products on Test Panels, as Method C. The Model 509/1 Film Applicator from Erichsen [*19*] may be fitted with any sort of drawdown bar or blade (see Fig. 8). Speed of the motion of the applicator may be preset, so the variation among several samples may be minimized.

Two devices Grenko [*3*] included with drawdown bars are more like bulk coating devices as they do not require putting down a puddle of coating before applying the blade. Indeed, these devices contain the coating and apply it to a stack of

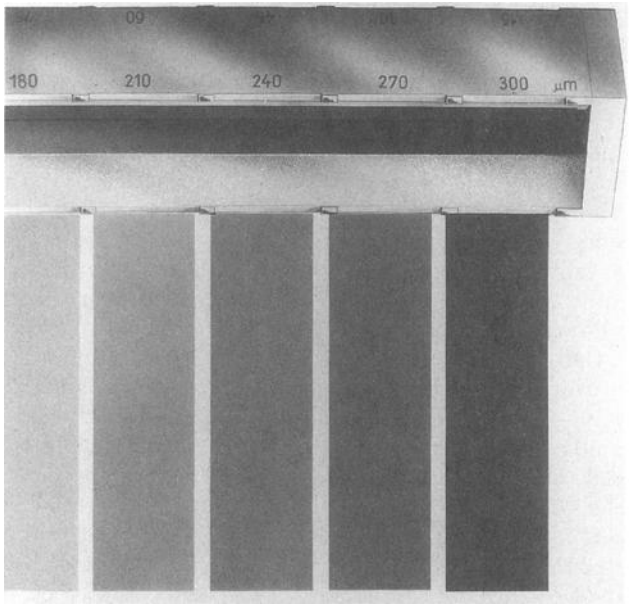

FIG. 7–*Multiple gap drawdown bar*—Six or eight gaps are machined along the same edge for casting side-by-side films for comparison. (Courtesy of Erichsen GMBH & Co.)

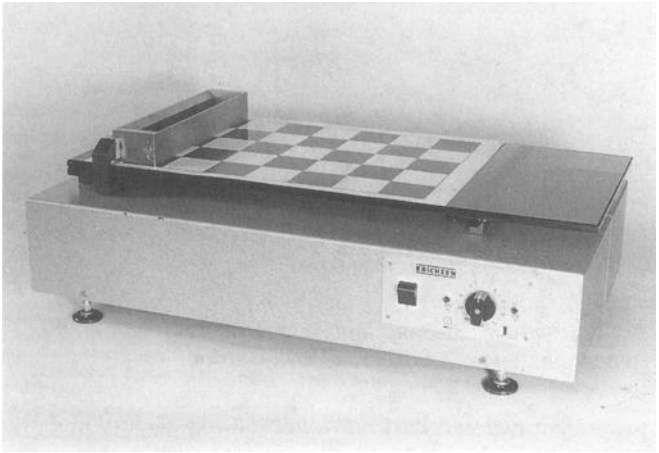

FIG. 8–*Electrically driven drawdown device*—Four speeds may be chosen to control drawdown rate. (Courtesy of Erichsen GMBH & Co.)

sheets, one sheet at a time as the sheets are pulled out from underneath the device. One such device is the Parks Film-O-Graph cylinder. One puts the cylinder on a stack of Leneta charts or metal panels, fills the cylinder with the coating, and pulls each sheet from underneath the cylinder. A portion of the rim edge of the cylinder is milled out to act as the gate to allow coating at a desired thickness. One may even use it for very viscous coatings (even putty) by forcing the fluid through the tube with a loose-fitting plug from the top and wiping the bottom of the tube over the substrate to be coated.

The second of the devices discussed was the Parks Rapid coater. Paper sheets were stacked in the bottom of a box with their ends out of a side slot at the bottom. The box was then filled with coating fluid, and each sheet was withdrawn individually. Grenko [*3*] noted this was not a precision device, but it was adequate for some purposes.

Grenko [*3*] also described the flat Parks Film-O-Graph, which used a flat plate with spring clips to hold shims along the sides of the sheet of substrate. One poured the coating onto the substrate between the shims and used a bar such as a ruler or other straight edge to doctor off the excess and make the coating as thick as the shims. Bending of the scraper bar by the very slightest amount would make very thin films almost impossible, but for thick films (for example, roof coatings), this technique worked well.

Some applicators are meant only for the wet film tests. Two especially useful applicators for these are the sag test devices and the wet hiding test devices. The latter, most frequently the Pfund Cryptometers (available from Erichsen [*19*] and Byk-Gardner [*20*]), have black or white glass (ceramic) beds over which a transparent wedged cover levels the coating film (see Fig. 9). Although these devices are quite hard, care in cleaning will assure they do not get scratched. They must be stored carefully, wrapped, and covered.

The sag test film casters essentially drawdown several narrow films in gradations of film thickness. Many are simply slotted U-shaped drawdown bars with variations in slot depth from 1 to 6 mil, 3 to 12 mil, and 14 to 60 mil. However, the New York Paint Club Technical Committee designed a special "leveling test blade" that had double slots for each depth

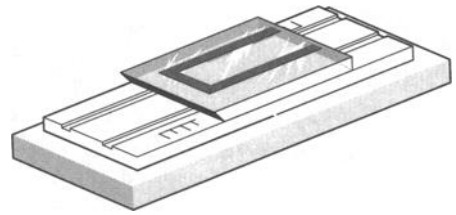

FIG. 9–*Pfund crytometer*—The white style shown is for black/dark paints, while a similar black style is used for white/light paints. (Courtesy of Byk-Gardner Inc.)

with a wide space between each set of double slots [*21*]. Their slots are 1, 2, 4, 8 and 16 mil in depth (see Fig. 10).

As paint film drip or sag depends on the rheological characteristics, the thickness of the coating that first sags may be related to the gravity-applied shear stress by the outer elements furthest away from the substrate on that film. Other rheological factors (high shear viscosity, ca. 10 000 s^{-1}, for instance) are also important in sag and leveling. Sag test devices complying with ASTM D 3730, Guide for Testing High-Performance Interior Architectural Wall Coatings, and several federal specifications and the New York leveling test blades are available from P. N. Gardner [*20*] and Byk-Gardner [*18*].

Wire-Wound Rods

For very thin films, the wire-wound rods are quite useful for quickly and easily applying films. The wire-wound rods are simple rods of 12 or 16-in. (30 to 40-cm) length, of ¼, ⅜, or ½ in. (0.63, 0.45, or 1.27 cm) diameter, with a sprial wind of wire tight about 75 to 80% of the rod. Table 2 shows a selection of wet film thicknesses obtained from the rods with different wire diameter.

The film laid down with a wire-wound rod is almost exactly a tenth the thickness of the wire winding. Strictly speaking, as the film has the rod depart, there are ridges in the film in the direction of travel of the rod. However, these collapse to make a quite smooth film unless there is rheological inhibition in the formulation or the coating is very fast drying. This technique is quite effective to simulate paper or can coating end products. There are industrial production systems that em-

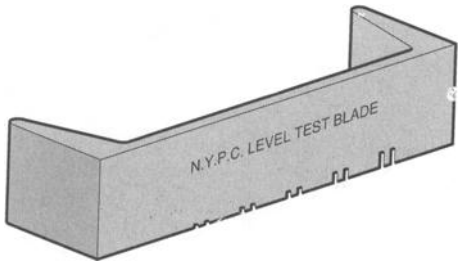

FIG. 10–*New York paint club leveling test blade*—The slotted blades are for assessment of sag and leveling. (Courtesy of Byk-Gardner Inc.)

TABLE 2—Selected coating thicknesses from wire wound rods.

Wire		Wet Film Thickness	
Size	Diameter (in.)	Mils	Micrometers
2.5	0.0025	0.25	6.4
3	0.003	0.3	7.6
3.5	0.0035	0.35	8.9
4	0.004	0.4	10.2
4.5	0.0045	0.45	11.4
5	0.005	0.5	12.7
5.5	0.0055	0.55	14.0
6	0.006	0.6	15.2
10	0.01	1.0	25.4
20	0.02	2.0	50.8
30	0.03	3.0	76.2
40	0.04	4.0	101.6
50	0.05	5.0	127.0
60	0.06	6.0	152.4
70	0.07	7.0	177.8
80	0.08	8.0	203.2
90	0.09	9.0	228.6

ploy wire-wound rods to meter coatings onto roll substrates, as well.

A similar device called the "spiral-film applicator" is available from Erichsen [*19*]. It is a wire-wound rod with a perpendicular handle (see Fig. 11). It is available to apply film thicknesses from 10 to 200 μm in widths of 80, 150, or 220 mm. Byk-Gardner offers a handle that attaches to the ends of the wire-wound rod for lab film preparation as well [*18*]. The Accu-Lab™ Lab Drawdown Machine has a rod holder and substrate holder to assure precision in laboratory manual film preparation [*22*].

There are also two-wire rods in which a second, smaller wire is wound in the grooves made by the first winding wire. These yield higher application rates than do the single-wound wire rods. There is potentially an advantage to the two-wire rods since they leave a different pattern in the coating. The ridges left are larger and may level faster and uniformly.

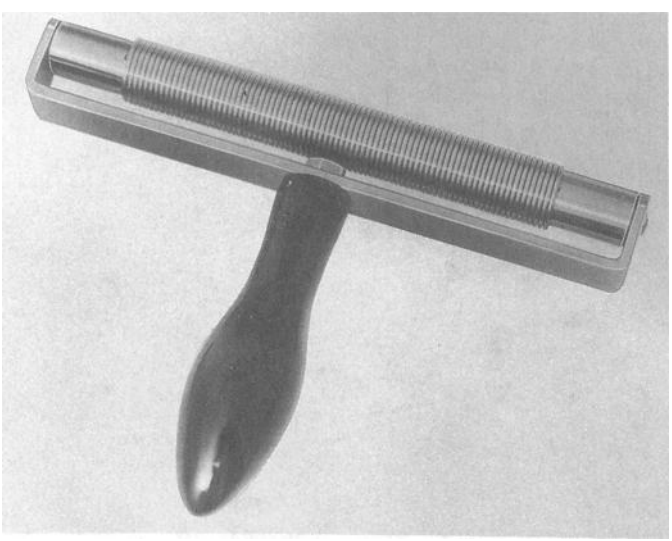

FIG. 11—***Spiral wire drawdown applicator***—**The handle shown grips the end of the wire-wound rod for application with one hand. (Courtesy of Erichsen GMBH & Co.)**

Spray Outs

Spray application, including by weight on a panel hanging on a balance in a spray booth, can be done with good precision. Good spray out application on panels can be done by those skilled in the art. To control the weight applied in a spray booth, a triple beam balance may be attached to a beam 5 or 6 ft. (1.5 or 1.8 m) above the floor, and a hanger-wire panel holder is hung from it as the spray target. A cardboard shield over the balance will keep off overspray. Tare the balance and preset weight needed to apply. Take off a few tenths of a gram to give a pointer indicator warning when the spray has almost reached the desired weight. Spray quickly to minimize evaporation.

There are automated spray devices. Grenko [*3*] related the automated spray device design from Bell Labs [*23*] to Method A of ASTM D 823. The Bell Labs design has the gun travel over stationary panels, while an alternative design has the panels on a moving belt under a stationary spray gun, similar to a design reported from Battelle [*24*]. In either case, the amount of coating applied to the panel is controlled by the speed of the moving belt and by nonvolatile content of the sprayed fluid. Grenko [*3*] notes the sample panels on the moving belt may be held to the belt with magnets or suction cups. Erichsen [*19*], Gardner [*20*], and others offer automated spray applicators for lab sample preparation (see Figs. 12 and 13).

The spray technique is particularly important, but precautions are necessary to assure evenness of coating on the substrate. The spray pattern should extend beyond the edges of the substrate when the nozzle is aimed at the center of the target. The spray pattern—be it flat, fan, or circular—has less paint at the edges than at the center. Moving the spray nozzle across the target or the target under the center of the nozzle makes the deposition more likely to be consistent in thickness.

Dip Coating

Dip coating is particularly important in some special cases. For instance, the edge protection of corrodible panels in preparation for the application of a test coating is a common practice. The Golden Gate Society for Coatings Technology Technical Committee use a red lead vinyl ½-in. (1.27-cm) dip for edge protection of their exposure panels quite successfully, as attack corroded only the desired exposure surfaces [*25*]. The point is that dipping assures film thickness without holidays that other techniques do not. This is particularly true for odd-shaped test specimens such as fragments of a pressurized gas cylinder in an unpublished Mellon Institute corrosion study.

Grenko [*3*] briefly reviewed two-dip coaters. Bruins [*26*] first designed one using a tire pump and needle valve to control the rate of panel withdrawal from the coating, while Payne designed an electric motor-driven device adopted for ASTM D 823 Method B. A commercial lab device is available from P. N. Gardner [*20*], with variable withdrawal speeds at 2 to 20 in. (5 to 50 cm) per minute. It can dip a panel of up to 2 lb (0.9 kg) and 1 ft^2 (0.3 m) in area (12 by 12 in. (3.65 by 3.65 cm).

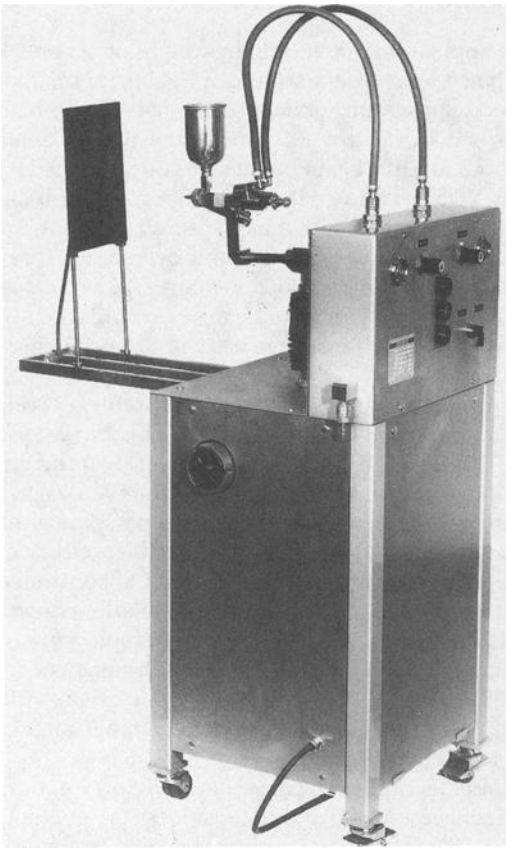

FIG. 12–*Single setting lab spray applicator.* (Courtesy of Erichsen GMBH & Co.)

FIG. 13–*Programmable lab spray applicator.* (Courtesy of Erichsen GMBH & Co.)

Again, care must be taken while dip coating. Film thickness control is a battle between wetting surface forces and the shear forces of drainage through the thickness of the film. Drip edges on the bottom edge may be avoided to some degree by having the panel holder inverted to hold the bottom edge upward for a portion (or intermittent portions) of the drying period.

Spin Coating

Grenko [*3*] described the work of Walker and Thompson [*27*] attaching a panel to a turntable and rotating for 1 min at 300 rpm to obtain a 25-μm varnish film thickness. He also described the Sward-Gardner [*28*] relation of film thickness (F) to viscosity (V, in poise) and nonvolatiles, % N, as

$$F = 0.4N + V^4 + 3$$

where spin rate was 290 rpm for 60 s. Their work had a precision of 5 to 10%, and corrections for time or rpm variations were offered. Parker and Siddle [*29*] suggested modifying the method by adjusting viscosity to equivalence for all fluids to be compared and using volume solids rather than weight percent nonvolatiles. Plots of film thickness versus volume percent nonvolatile were straight lines for non-thixotropic fluids, but curvature existed for thixotropic fluids.

A commercial lab spin coating device is currently available from Erichsen [*19*]. There are two versions, one with 600 rpm speed set, and another adjustable from 50 to 2000 rpm (see Fig. 14).

OTHER TIPS ON PRACTICE OF THE ART

Dust is always a problem, especially in formulation labs that have pigment dusting in the lab and plant. Cover cast

FIG. 14–*Lab spin coating device.* (Courtesy of Erichsen GMBH & Co.)

films immediately to keep the dust off. The easiest cover is the top of a box from a typewriter paper or file folder shipment container. Simply cut out ½ in. (or 1 cm) strip from two, three, or four sides for free flow of air. Of course, a similar cover can be made from this plywood. Keep the cover on top of the lab refrigerator or book shelf so it's always at hand.

Make sure the film is drying under appropriate temperature and humidity conditions. Something in the formulation may respond in an adverse manner to condensing moisture that can form droplets on the surface as evaporating solvent rapidly cools the system. In moisture-cure and reactive two-package urethanes, the condensing moisture may react with the isocyanates to modify degree of cure, which can reduce strength, solvent resistance, etc. In systems that do not react with the condensing water, one may still get pits, pinholes, or haziness from the condensing water droplets on the surface. Paint applicators are learning to pay attention to humidity variation and its effects on the end product surface.

CONCLUSION

How the film is prepared for testing can have a dramatic effect on the test results. The thought put into film preparation prior to preparation and the care used in casting can be crucial factors in obtaining meaningful and reproducible results.

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38

Measurement of Film Thickness

by C. M. Wenzler[1] and J. F. Fletcher[1]

ONE OF THE MAJOR REQUIREMENTS OF PAINT and coating testing is the measurement and control of film thickness. Ensuring that a specification is achieved is important in laboratory tests, paint application, automatic spraying, and other coating application methods.

A number of test methods are available, and the choice is dependent on: (1) the location—laboratory or site; (2) the material coated—metal (ferrous or nonferrous), wood, plaster, brick and plastic; (3) the condition of the coating—wet or dry; and (4) the condition of the surface—rough or smooth, flat or shaped, thick or thin, etc.

WET FILM THICKNESS

The measurement of wet film thickness provides the first opportunity to check the coating and its application process. It also offers an assessment of the spreading rate when a paint is applied. It is very important that wet film measurements are made as soon as the coating is applied to avoid error due to solvent loss during the curing process.

Reference to the technical data for volume solids in the coating is required to establish the wet and dry ratio so that wet film thickness values can be converted to dry film equivalents. In most cases wet film thickness gages can be cleaned with solvents and reused.

ASTM Test Methods for Measurement of Wet Film Thickness of Organic Coatings (D 1212) standardizes the Inmont wet film gage (formally known as Interchemical and commonly known as the wet film wheel) and the Pfund wet film gage. These two gages are detailed in the following sections, and two nonstandardized methods are also described.

Inmont Wet Film Gage (Wet Film Wheel)

The Inmont wet film gage consists of two concentric outer disks with an inner eccentric disk with a smaller diameter positioned between them as shown in Fig. 1. The outer disks are scaled, with the clearance between the inner disk and the outer disk from zero to a maximum value as shown.

The gate is used as follows. The disks are placed with the maximum clearance on the specimen of coating and rolled toward the minimum clearance in either direction. The paint will coat the inner disk until the clearance is greater than the wet film thickness. The point at which the coating stops on the inner wheel is referenced to the scale on the outer wheel and the value noted.

Starting from maximum value avoids the possibility of pushing paint ahead of the inner disk, creating an error condition when the gage indicates a value higher than the true wet film thickness.

A number of ranges are available.

Pfund Wet Film Gage

As shown in Fig. 2, this gage consists of a convex lens, L, whose radius of curvature is 250 mm, at the lower end of tube T1 that slides in the outer tube T2. Compression springs, S, keep the lens out of contact with the paint film until pressure is applied on tube T1. In making a measurement, the gage is placed on the painted surface and the lens is pushed slowly through the film until stopped by the substrate. The pressure is released, and the diameter of the spot of paint transferred to the lens is measured. A 1 to 1 ratio for the thickness added by the paint displaced by the lens to the actual thickness has been assumed and is accounted for in the equation

$$t = D^2/16R \tag{1}$$

where

D = diameter, mm, of spot, and
R = radius of curvature, mm, of the lens.

Table 1 gives film thickness and the corresponding spreading rate in square feet per gallon for spots from 3 to 38 mm in diameter.

It has been observed that a substantial proportion of paints do not obey the 1 to 1 relationship. The actual thickness, obtained by independent methods, may be several times, or only a fraction of, the thickness calculated by the equation. A small amount of thinner added to a paint may increase the diameter of the spot on the lens and give a corresponding increase in the calculated thickness. This phenomenon has been ascribed to the effects of surface tension. Hence, for best results, a correction factor should be established for each type of paint based on the known thickness of a freshly prepared film measured by the Inmont gage.

Reproducibility is within about 2% for films 2 mils (50 μm) thick, decreasing to about 10% for films 5 mils (125 μm) thick, then becoming better as thickness increases.

[1]Elcometer Instruments, Ltd., Manchester, England.

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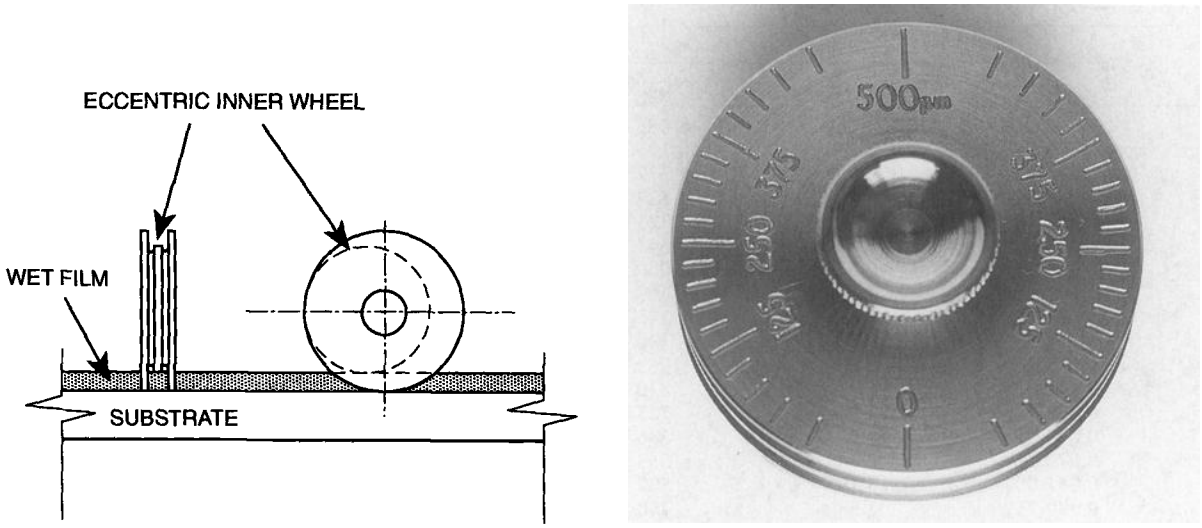

FIG. 1–Inmont gage (Interchemical) wet film wheel *(left)* and 120 photo *(right)*.

Notch Gages (Wet Film Comb)

Notch gages are formed on the edge of a piece of material so that each notch has a different clearance from the reference shoulders to its neighbors (Fig. 3). Many different materials are used, such as stainless steel, aluminum, and plastic in a variety of shapes: square, rectangle, triangle, hexagon, etc. It should be noted that combs made of aluminum are known to wear on rough surfaces. It is a simple low-cost device which is useful when approximate values are satisfactory as the notches have discreet values and are not continuous. The gage is dipped vertically into the film until the reference shoulders are resting firmly on the substrate. The thickness of the film is between the highest coated notch face and the next highest notch value.

Several different methods of manufacture of these gages exist from spark-eroded stainless steel precision combs, through punched aluminum sheet, to plastic flow molded combs. The stainless steel combs can be certified with measurements of the tooth displacements, which are traceable to national standards. As the stainless steel is hard wearing, this certificate can be valid over a period of up to one year. On the other hand, plastic combs, although manufactured from solvent-resistant ABS plastic, should only be used once as the solvent in the coating may soften the plastic. Plastic combs can be tagged and kept as a permanent record of wet film measurement.

Aluminum combs are prone to wear, and the condition of the gage should be monitored before use.

Gages are available in many ranges, from 0.5 mil (2.5 μm) to 160 mils (4 mm/4000 μm) (for high-build, low-solvent-content coatings). The teeth are normally square ended, but for thicker coatings pointed teeth are often used.

Notch gages are supplied by various coating equipment suppliers, e.g., Nordson, Elcometer Inc. and are described in ASTM Practice for Measurement of Wet Film Thickness of Organic Coatings by Notched Gages (D 4414).

Needle Micrometer

This method was used to study the relationship between the clearance of a doctor blade and the thickness of the wet film left by the blade [*1*]. A needle is attached vertically to the objective holder of a microscope. The barrel is lowered until the needle just touches the film that has been spread on a plain metal panel. The contact is observed through a horizon-

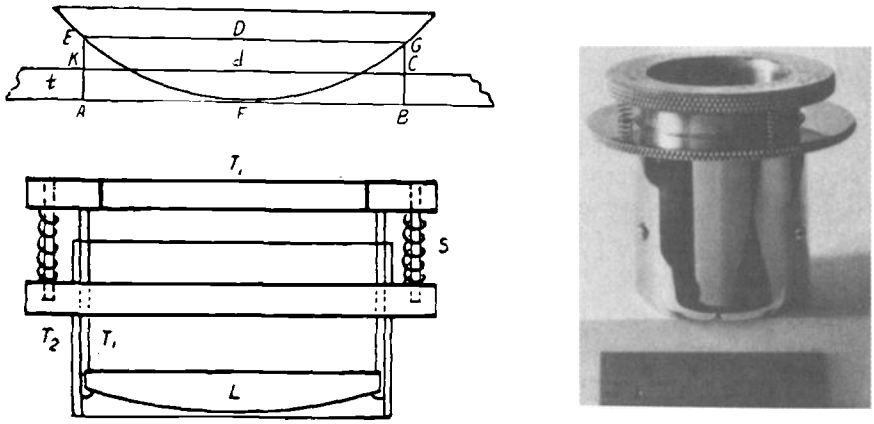

FIG. 2–Pfund gage *(left)* and photo *(right)*. (Figure taken from previous edition of this manual.)

TABLE 1—Spreading rate by Pfund film gage.

Diameter of Spot, mm	Thickness		
	mm	Mils	Ft/Gal
3	0.002 25	0.089	18 088
4	0.004 00	0.157	10 175
5	0.006 25	0.246	6 512
6	0.009 00	0.354	4 522
7	0.012 25	0.482	3 321
8	0.016 00	0.630	2 543
9	0.020 25	0.805	2 009
10	0.025 00	0.985	1 628
11	0.030 25	1.19	1 345
12	0.036 00	1.42	1 130
13	0.042 25	1.66	963
14	0.049 00	1.93	830
15	0.056 25	2.21	723
16	0.064 00	2.52	636
17	0.072 25	2.84	563
18	0.081 00	3.19	502
19	0.090 25	3.55	450
20	0.100 00	3.94	407
21	0.110 25	4.34	369
22	0.121 00	4.76	336
23	0.132 25	5.20	307
24	0.144 00	5.67	282
25	0.156 25	6.15	260
26	0.169 00	6.65	241
27	0.182 25	7.18	223
28	0.196 00	7.72	207
29	0.210 25	8.28	193
30	0.225 00	8.96	180
32	0.256 00	10.08	158
34	0.289 00	11.38	141
36	0.324 00	12.76	125
38	0.361 00	14.21	113

tal microscope (Fig. 4). When contact is made, the needle and its image reflected by the film just meet. The needle is then lowered into the film until it just touches the metal panel. This contact is noted by the deflection of a galvanometer in series with the panel, a dry cell, and the needle. The thickness of the film is calculated from the number of turns made by the focusing screw of the vertical microscope between the two points of contact.

It should be noted that this technique is only applicable to measurements made in a laboratory as it is impractical for work on site.

DRY FILM THICKNESS (DESTRUCTIVE METHODS)

As there are many circumstances under which coatings and paints are used, no single method of dry film thickness measurement is universal. Some methods are destructive, and these are most often used when nondestructive methods are not applicable. The nondestructive methods are limited to coatings on metals.

Micrometers and Dial Gages

When a chip or flake of coating is freed from the surface of the coated object, its thickness can be measured directly using a micrometer. Alternatively, the total thickness of the substrate and coating can be measured; the substrate can then be remeasured after removing the coating with a scraper or solvent. The coating thickness is then the difference between the two measurements.

ASTM Test Method for Measurement of Dry-Film Thickness of Organic Coatings (D 1005) details a preferred procedure using a dial micrometer mounted on a support with a clamp to hold the specimen (see Fig. 4). This method is recommended only for thicknesses over 0.5 mil and is accurate ±0.1 mil.

A hand-held dial gage, the Elcometer Model 126 (Fig. 5), may be used. In this case the dial records the difference in position between the foot that sits on the surface of the coating and the stylus with its ball end, which passes through a hole prepared in the coating to the surface of the substrate. This is particularly useful for site work. However, for best accuracy and precision, the firmly mounted dial gage specified in ASTM Method D 1005 is preferred.

Gardner Needle Thickness Gage

This instrument is designed to measure the thickness of electrically nonconducting films on metal (conducting) substrates. It is small enough to be used in the field where the substrate can be made part of the electric circuit. The needle makes only a minute puncture in the film. In many instances, particularly in a go no-go determination, the damage is so slight that the method may be considered nondestructive for many end users.

The case aluminum housing contains the needle screws for forcing the needle through the film and a lamp to signal when the needle contacts the substrate. For use in the field and for occasional use in the laboratory, the electric circuit comprises the needle, the substrate, a dry cell, the lamp, and a cord that connects with the substrate. In the laboratory, if many measurements are to be made, it is advisable to use a step-down transformer and to connect to a 110-V source.

The thickness is read on a dial attached to the screw. One turn of the dial raises or lowers the needle by 2 mils. The dial is graduated in steps of 0.05 mil. Range is 0 to 15 mils.

The zero setting of the needle is obtained by retracting the needle within the housing, placing the gage on a plane metal block, and lowering the needle until the lamp signals contact. The block is replaced by the specimen, and the needle is lowered until the lamp again signals contact. The difference between the two readings is the thickness of the film.

Gardner Carboloy Drill Thickness Gage

In many instances films are so hard that they successfully resist penetration by the needle penetrometer described above. This difficulty has been overcome by substituting a Carboloy drill for the needle. The drill is a needle terminating in a pyramid having three faces. The drill is secured in a chuck that can be rotated and advanced independently. The rotation is controlled by finger action on a knob at the upper end of the chuck shaft. In all other respects, the operation is the same as that of the needle gage.

This method has been standardized by ASTM as Procedure B in Test Method for Measurement of Dry Film Thickness of Non-metallic Coatings of Paint, Varnish, Lacquer, and Related Products Applied on a Non-magnetic Base (D 1400).

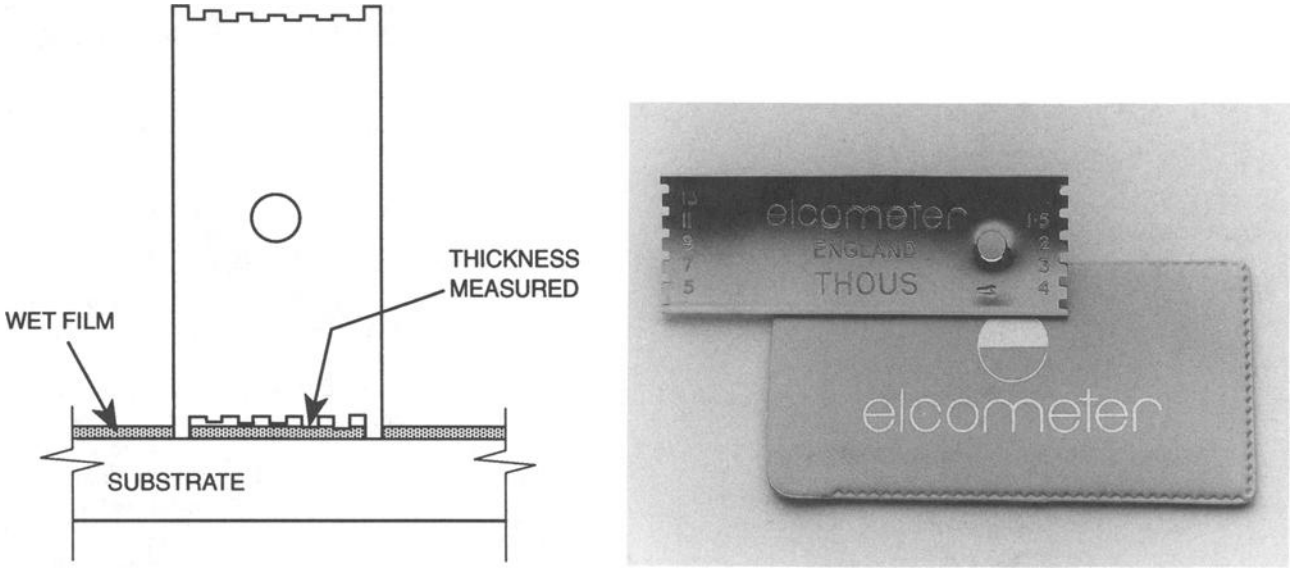

FIG. 3–Wet film comb 115 and photo.

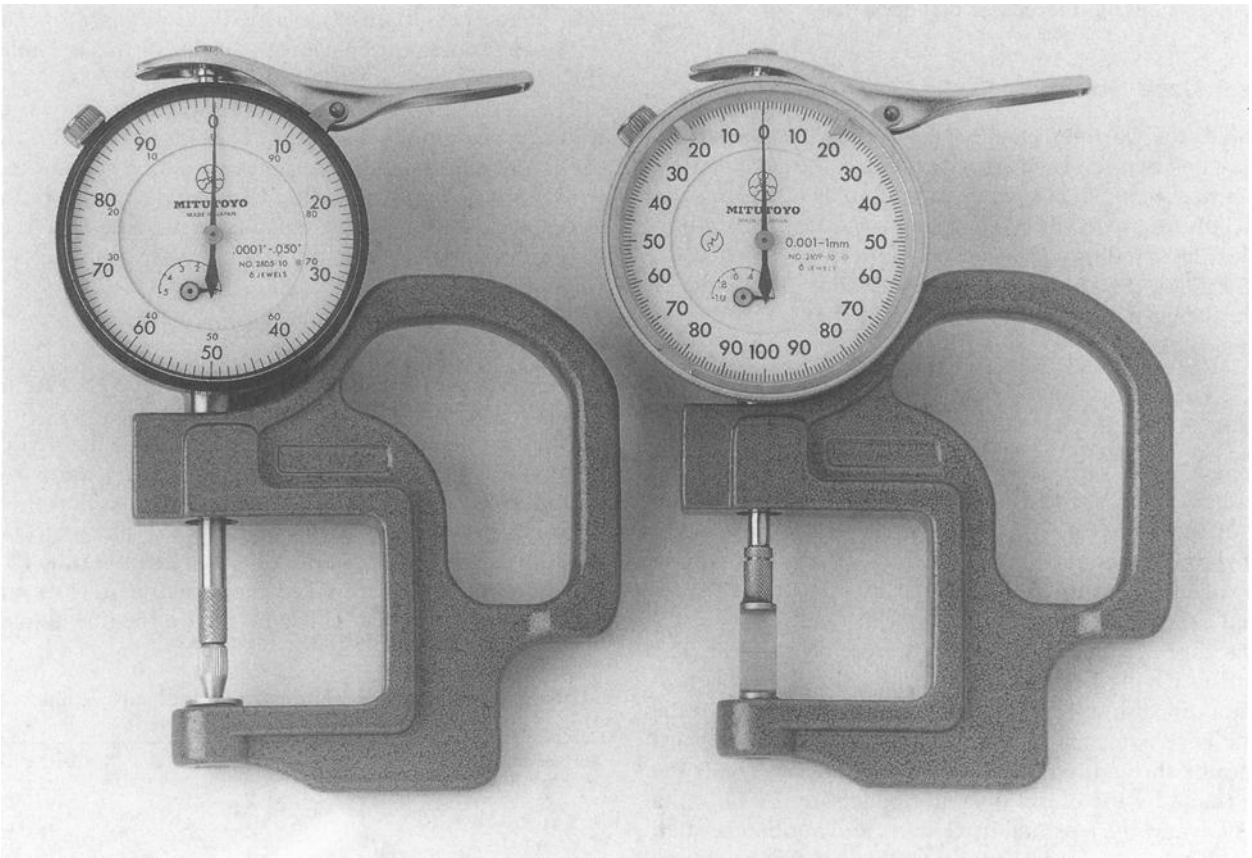

FIG. 4–Dial micrometer.

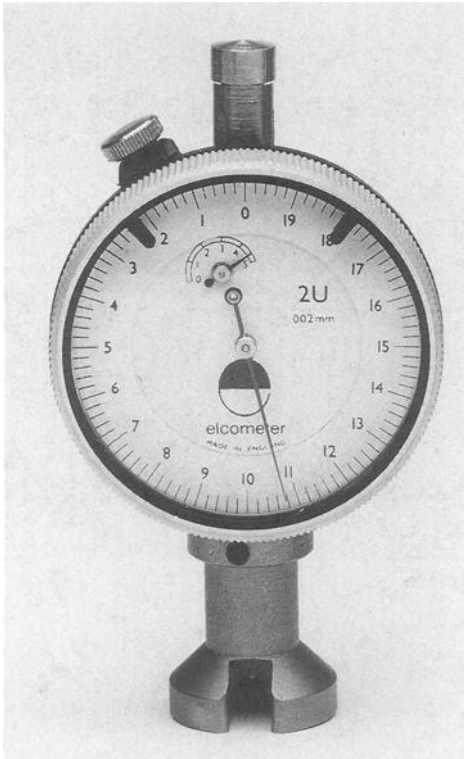

FIG. 5–Elcometer dial gage 126.

Gardner Gage Stand

Although the Gardner needle gage and the Carboloy drill gage may be operated by manually holding the gage against the specimen, using the Gardner gage stand is less tiring and more accurate, especially when many measurements are to be made. The stand provides constant known pressure [up to 10 lb (5 kg)] on the specimen and ensures that the needle or drill are always perpendicular to the specimen.

Gardner Micro-Depth Gage

Although in outward appearance this gage resembles the gages described in the last two subsections, only the establishing of the zero setting is the same. Measurement is not restricted to nonmetallic films on metal—any type of film on any type of substrate may be measured, and the film is always damaged.

In this gage, a chisel replaces the needle of the gage. The zero setting having been established, the chisel is advanced by an amount estimated to be less than the thickness of the film. The gage is placed on the specimen and drawn toward the operator through a distance of a few millimetres. If the scratch made by the chisel does not penetrate the film, the chisel is advanced by a small increment, and another scratch is made. The procedure is repeated until the substrate is reached and exposed. Inspection is best made with the aid of a low-power magnifier. The range is 0 to 40 mils (1000 μm). Repeatability depends on the magnitudes of the increments and the compressibility of the film and substrate. For example, specimens with poor adhesion may be torn off, exposing the base, even if the chisel does not penetrate the film.

Microscope for Film Thickness

Classical Method

To use a microscope to assess film thickness, a section is prepared and the width of the coating is measured using a graticule in the eyepiece of the microscope. For an approximate assessment, a flake of the coating can be used, but for best results from this method the specimen should be prepared as follows.

The specimen is mounted in a block of wax. The face of the mount is cut or ground to a smooth surface. The prepared specimen is then inspected under the microscope. ASTM Method for Microscopic Measurement of Dry Film Thickness of Coatings on Wood Products (D 2691-88) is based on this method; however, as paints are often hard and brittle, a grinding and polishing method is preferred to the blade method indicated in D 2691.

Brightwell Method [2]

This method does not require removal of a chip and elaborate mounting and preparation. A tiny furrow is made in the film or a small chip is removed. A prism or ribbon of light is projected on the selected area at an angle of 45°. The distortion of the beam is examined with a microscope equipped with a micrometer eyepiece. Apparatus for this is available in the Schmaltz optical surface analyzer (Carl Zeiss).

The apparatus is calibrated by measuring known depths milled in a smooth metal block. The ribbon of light is focused on line A, and the filar micrometer reading is recorded. The procedure is repeated on line BC. The difference multiplied by the calibration factor equals the thickness of the film. Table 2 compares results by this method with results with a micrometer.

Stopped Method [3]

A cut is made in the film with a sharp knife. The microscope is focused, in turn, on the upper and lower edges of the cut. The thickness of the film is computed from the vertical adjustments of the microscope. If the value is not known, it may be found as follows: Put a piece of plate glass on the stage. Lower the tube until it just touches the plate. Record the reading of the fine adjustment. Now raise the tube as far as possible and again record the fine adjustment. Now raise the tube as far as possible and again record the fine adjustment.

TABLE 2—Film thickness (mils) by optical surface analyzer and dial micrometer (Brightwell).

Surface Analyzer	Dial Micrometer
0.39	0.4
0.46	0.5
0.71	0.8
0.98	1.0
1.30	1.3
1.51	1.4
2.28	2.1
3.58	3.5

The distance of the tube from the plate divided by the number of turns of the adjusting screw gives the value for each turn.

Tooke Inspection Gage (Paint Inspection Gage P.I.G.) [4]

This gage (shown in Fig. 6) provides for estimating the thickness of a film from the geometry of a V-groove cut in the film by a special tool. With the aid of a ×50 illuminated magnifier equipped with a reticle in the eyepiece, the operator measures the lateral distance from the top edge of the cut and the projection of the intersection of the cut and the substrate. To make a measurement, a "bench mark" of ink applied to the surface of the film serves to make the top edge of the cut readily visible. A short cut is then made at a right angle to the bench mark with the selected cutting tip. Film thickness is then obtained by counting the scale divisions as described previously.

The relationship among the tips is summarized in Table 3.

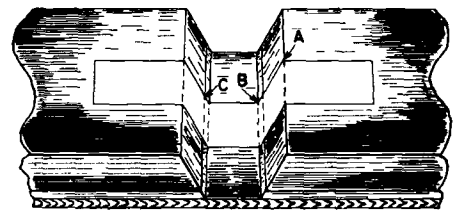

FIG. 6–Groove in paint film.

TABLE 3—Tooke inspection gage tip specifications.

Tip	Maximum Coating Thickness, mils	Precision of Thickness Determination Represents, mils	One Division on Reticle Scale, mils
×1	50	±0.25	1.0
×2	20	±0.13	0.5
×10	3	±0.025	0.1

Saberg Drill

This method is similar to the Tooke inspection gage described in the previous subsection; however, a circular drill is used to penetrate the film. The hole can then be inspected using the ×50 magnifier with graticule, and the width of the cut from the outer edge to the print where the drill penetrates to the substrate is a measure of the coating thickness. For the instrument kit supplied by Elcometer Inc., Rochester Hills, MI 48309 (Model 195), the calculation of coating thickness is as follows:

1. For measurement in mils, multiply graduations by 0.79.
2. For measurement in micrometers, multiply graduations by 20.0.
3. This method is now described in ASTM Test Method for Measurement of Dry Film Thickness of Protective Coating Systems by Destructive Means (D 4138).

DRY FILM THICKNESS (NONDESTRUCTIVE METHODS)

Permanent Magnet Thickness Gages

Permanent magnet coating thickness gages can be used to determine the thickness of films applied to magnetic substrates such as steel, iron, magnetic stainless steel, etc., providing that the coating is nonmagnetic. Materials such as nickel and cobalt, that are naturally magnetic have to be treated with care, while paints containing magnetic particles, such as some ferrous micaceous iron oxide (MIO), can cause errors when using magnetic gages.

Simple magnetic coating thickness gages or mechanical gages use the principle that the attractive force between a permanent magnet and the magnetic metal substrate is inversely proportional to the distance between them.

The principal limitations are (1) the film must be sufficiently hard to prevent indentation, and (2) the film must not be tacky causing the magnet to be held by the surface of the coating.

Electronic magnetic coating thickness gages are also available, but these will be described in a separate section entitled **Electromagnetic Thickness Gages;** however, this section does include the electronic gage based on the magneto-resistor probe.

Magne-Gage [5]

This instrument (Fig. 7) consists of a small permanent bar magnet, 2 mm in diameter, suspended from a horizontal lever arm. The arm is actuated through a spiral spring by turning a dial. The tip of the magnet is brought into contact with the paint film (on iron or steel), and the dial is then turned until the magnet is detached. The attractive force between the magnet and the film support is indicated on the dial, and the thickness of the nonmagnetic paint film is obtained from a calibration curve relating thickness to dial reading.

The gage can be used to measure coatings on convex and concave surfaces as well as on flat ones provided the radius of the curvature is not too small. Unless special calibrations are made, cylinders should not be less than ½ in. (1.27 cm) in diameter, spheres not less than ¾ in. (1.9 cm), and flat pieces should be at least ¾ in. (1.9 cm) square.

Magnets for thicknesses in the following ranges are available: 0.0 to 0.002, 0.002 to 0.007, and 0.007 to 0.025 in.

ASTM Method for Nondestructive Measurement of Dry Film Thickness of Nonmagnetic Organic Coatings Applied to a Ferrous Base (D 1186) has standardized the operation on the magne gage.

Hand-Held Magnetic Gages

These gages are being superseded by electronic gages, and some—such as the Tinsley gage and the chemigage—are no longer manufactured. However, many thousands of these types are still in use, so it is appropriate to describe them.

The simplest form of these gages contains a magnet suspended from a coil spring housed in a pen-style body manufactured from aluminum or plastic. A scale is drawn on the body and a marker used to indicate the extension of the spring on the scale. The reading on the scale when the magnet lifts off the surface corresponds to the thickness of the coating.

The scale on these instruments is nonlinear, leading to poor resolution at the maximum range, usually 20 mils (500 μm),

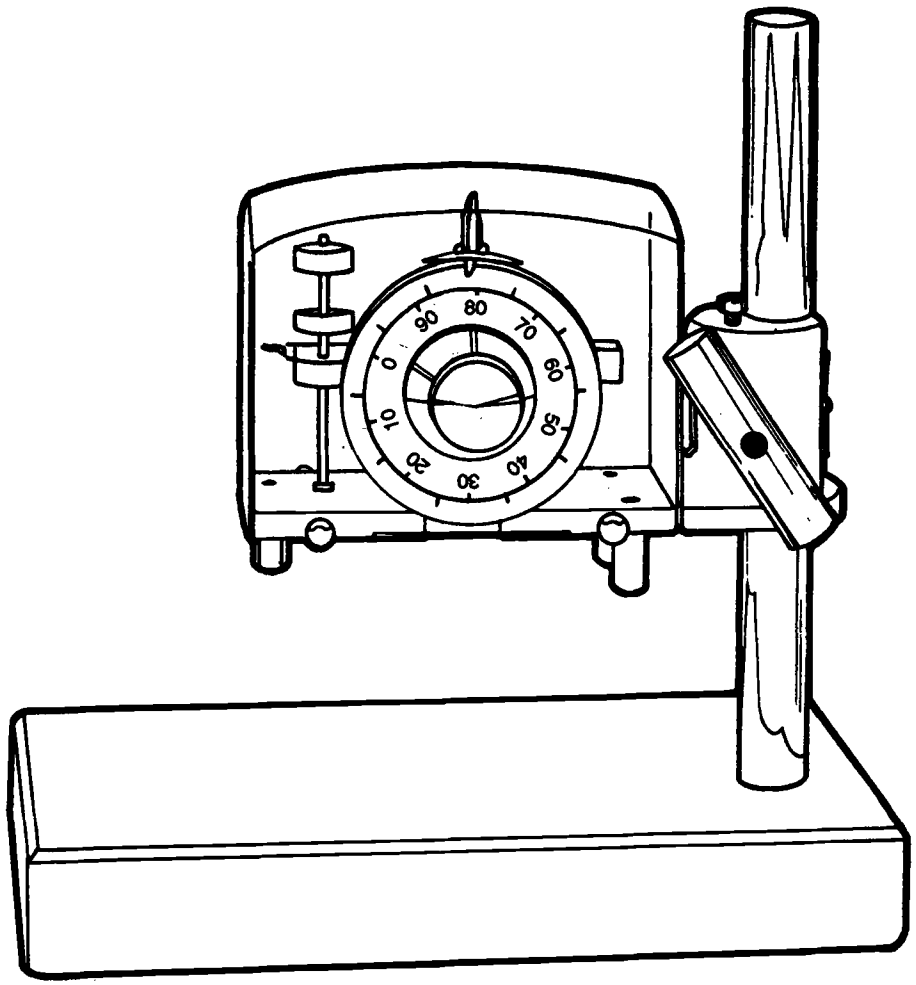

FIG. 7–Magne gage (courtesy of American Instrument Co.).

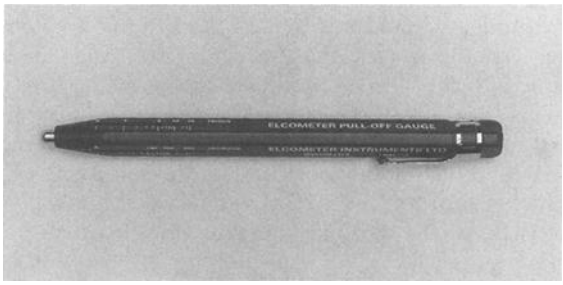

FIG. 8–Elcometer pull off gage 157.

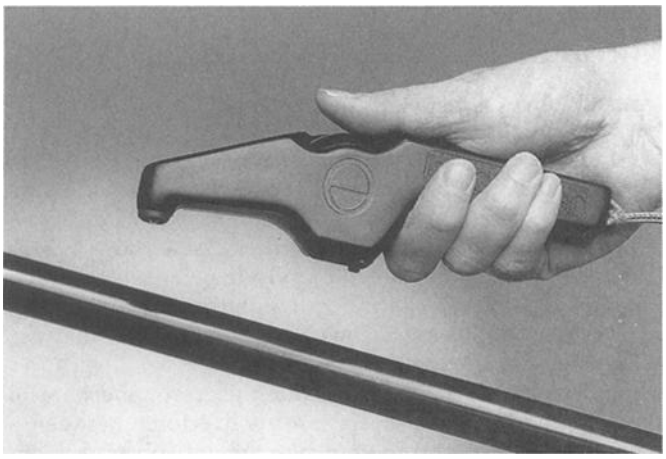

FIG. 9–Elcometer magnetic coating thickness gage 211.

and great care must be taken to ensure that they are used vertically to avoid the influence of gravity on the spring-magnet combination. Some of these types of gages have design features to overcome the gravity effect when the gage is used horizontally. An example of this type of gage is the Elcometer Model 157 (Fig. 8).

A common form of the hand-held magnetic gage is shown in Fig 9, and its principle is illustrated in Fig. 10. A balanced beam with a magnet fitted to one end and counterbalanced by a brass weight at the other is attached at the pivot to a helical spring. The other end of the spring is attached to a ring holding the scale. Rotation of the ring raises or lowers the magnet.

The gage is placed on the surface to be tested in any orientation as the balance weight ensures that gravity effects are neutralized. The ring or scale wheel is pushed forward

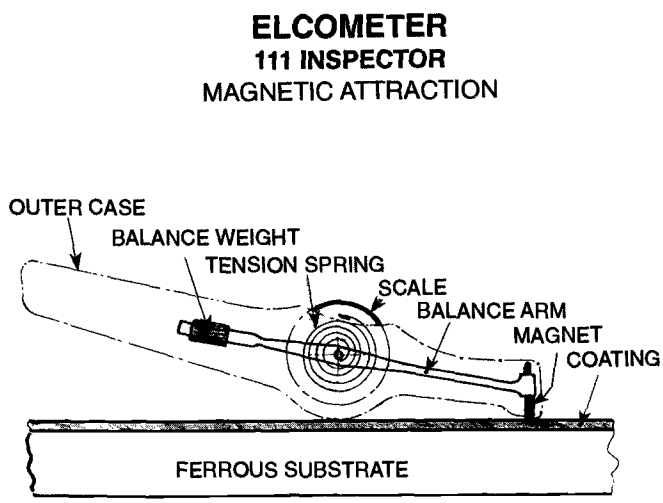

FIG. 10–Magnetic coating thickness gage principle.

(anticlockwise rotation) to bring the magnet in contact with the coating and to set the scale to a maximum reading. The ring or scale wheel is then rotated clockwise until the magnet breaks free, the thickness of the coating being indicated by a pointer.

This type of gage is calibrated against plated standards available from NIST, and accuracy against these standards of ±5% of reading are achieved. It should be noted that the steel used to make NIST standards is not always representative of engineering steels, and therefore a practical operating accuracy of ±10% is obtained in the field.

Elcometer (Model 101)

The Elcometer is one of the first magnetic thickness gages to be commercially available, being patented in 1948. Based on magnetic permeability, the magnetic flux acts on an armature suspended in between the two magnetic arms of the unit (Fig. 11) north and south poles. The turning moment of the magnetic flux is countered by a helical spring, and the magnitude of the magnetic flux changes with the distance between the ends of the magnetic arms (ball feet) and the substrate beneath the coating. A pointer attached to the armature indicates the thickness of the coating. Instruments covering ranges from 0 to 3 mil (0 to 80 μm) to 0 to 0.75 in. (0 to 18 mm) are available.

Magneto Resistor (Electronic)

This instrument combines a permanent magnet with a magneto-resistor in a probe to provide a signal which varies with the intensity of the magnetic field, which in turn is influenced by the distance of the magnetic substrate from the tip of the probe (Fig. 12).

The scale of the instrument is nonlinear and uses an analogue meter movement to indicate the thickness. In operation it is necessary to set zero on the uncoated metal and calibrate to a thickness of known value to obtain the best accuracy.

These instruments have been superseded by the electromagnetic induction types and by digital electronics, but again many instruments are in use and the principle embodied in the probe is still used for ferrite detection in stainless steel

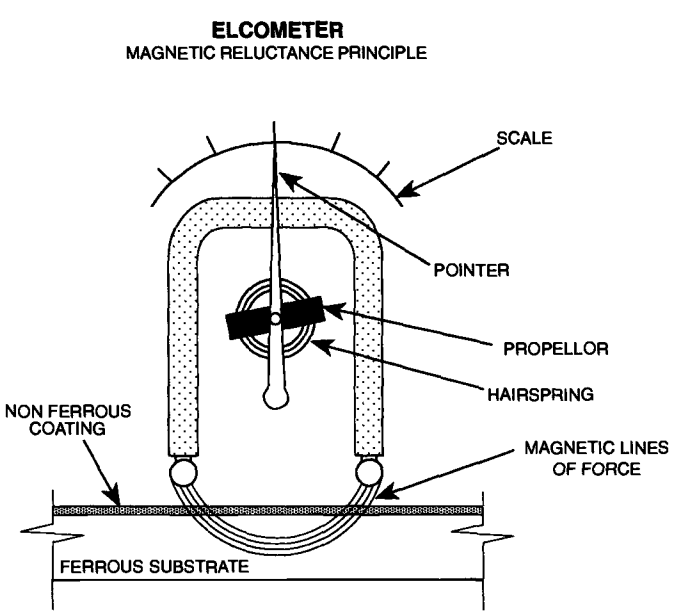

FIG. 11–Elcometer 101 principle.

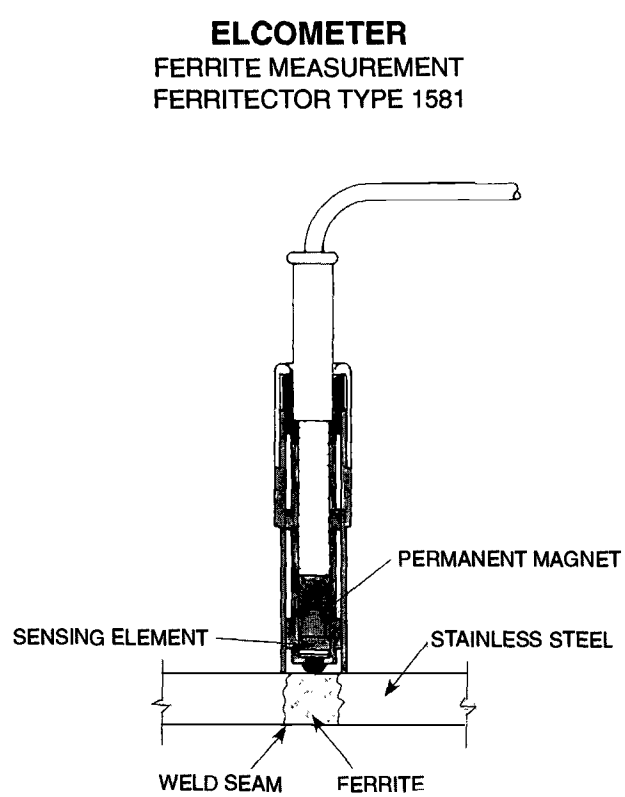

FIG. 12–Magneto resistor principle.

weld materials. In this application the magnetic properties of the substrate change with the ferrite content and the gage is calibrated in reverse, that is to say, zero, with the probe away from the influence of the magnetic material (free air) and maximum (Ferrite Number 28) on a 20 mil/thou in. (500-μm)-thick coating on a mild steel base.

For ferrite measurement, the probe is applied to an uncoated weld.

Electromagnetic Thickness Gages

The electromagnetic induction method for measuring film thickness is based on the effect of a magnetic metal substrate on the balance of the alternating magnetic field in the probe tip, generated in the probe (Fig. 13) by a signal applied to the central coil.

When the probe is away from the influence of the substrate (free air condition), the net voltage output from the two outer coils tends to zero. As the substrate is brought towards the tip, the field is increasingly out of balance between the two outer coils until, with the uncoated substrate in contact with the tip, the net voltage output from the coils tends toward V max.

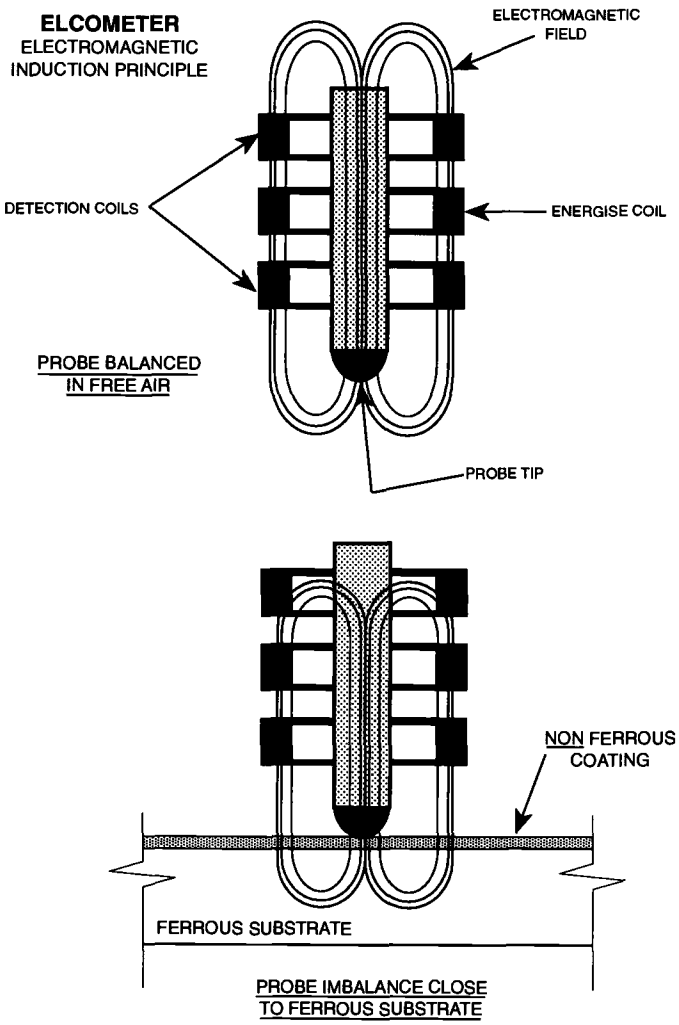

FIG. 13–Electromagnetic induction principle.

The voltage output from the probe can be amplified and calibrated and then used to display a thickness value. Three types of electronic coating thickness gages have been developed on the basis of this probe technology using analogue, digital, and microprocessor electronics. These types of gages have been standardized by ASTM as Test Method B of D 1186.

Analogue Electromagnetic Thickness Gages

The simplest form of instrument uses a nonlinear scale on a meter movement to display the voltage output from the probe in thickness terms. The Elcometer Model 145 (Fig. 14) is an example of this type of unit.

In common with most electronic coating thickness gages, the instrument must be calibrated by setting the needle to zero with the probe on the uncoated magnetic metal substrate and then setting the upper scale point using the calibration control with the probe on a known thickness of coating.

Two forms of thickness standard are in common use: (1) the plated type, as illustrated by the standards available from NIST and other sources, and (2) the measured and unmeasured plastic shims available commercially from gage manufacturers. In many applications the plastic shims are preferred as calibration on the work to be measured reduces the errors of calibration due to surface finish, curvature, and substrate composition. More details of this are given later in this chapter under **EFFECTS OF SURFACE FINISH, CURVATURE AND SUBSTRATE COMPOSITION ON ELECTROMAGNETIC AND EDDY CURRENT MEASUREMENTS.**

Digital Electromagnetic Thickness Gages

Advances in electronic components and instruments design techniques have made it possible to significantly reduce the size of coating thickness gages while returning and enhancing the features users find necessary. The use of digital electronics means that the voltage output from the probe can be converted to a numerical value early in the processing of the signal, thus reducing the effects of instrument temperature changes and component drift on the accuracy of the result. It is also possible to use a linear scaling, making it possible to have a fixed resolution over the full range of the instrument scale although resolutions are often enhanced in the 0 to 10 mil range (0 to 100 μm when scaled in metric units). An illustration of this type of instrument is shown in Fig. 15, but it should be noted that this type of product is already being superseded by microprocessor-based designs. The same principles of calibration apply to digital electromagnetic coating thickness gages as apply to the analogue types, and accuracy capabilities of ±5% of readings are achieved in the field.

Microprocessor Electromagnetic Thickness Gages

The development of microprocessor electronics and their application to portable coating thickness gages has made it possible to improve the accuracy and reproducibility of these instruments as well as allowing developments in range, special calibration techniques for rough surfaces, memory of readings, statistical calculation, and printouts.

In a microprocessor design, the characteristic of the probe voltage output against coating thickness value is stored in the

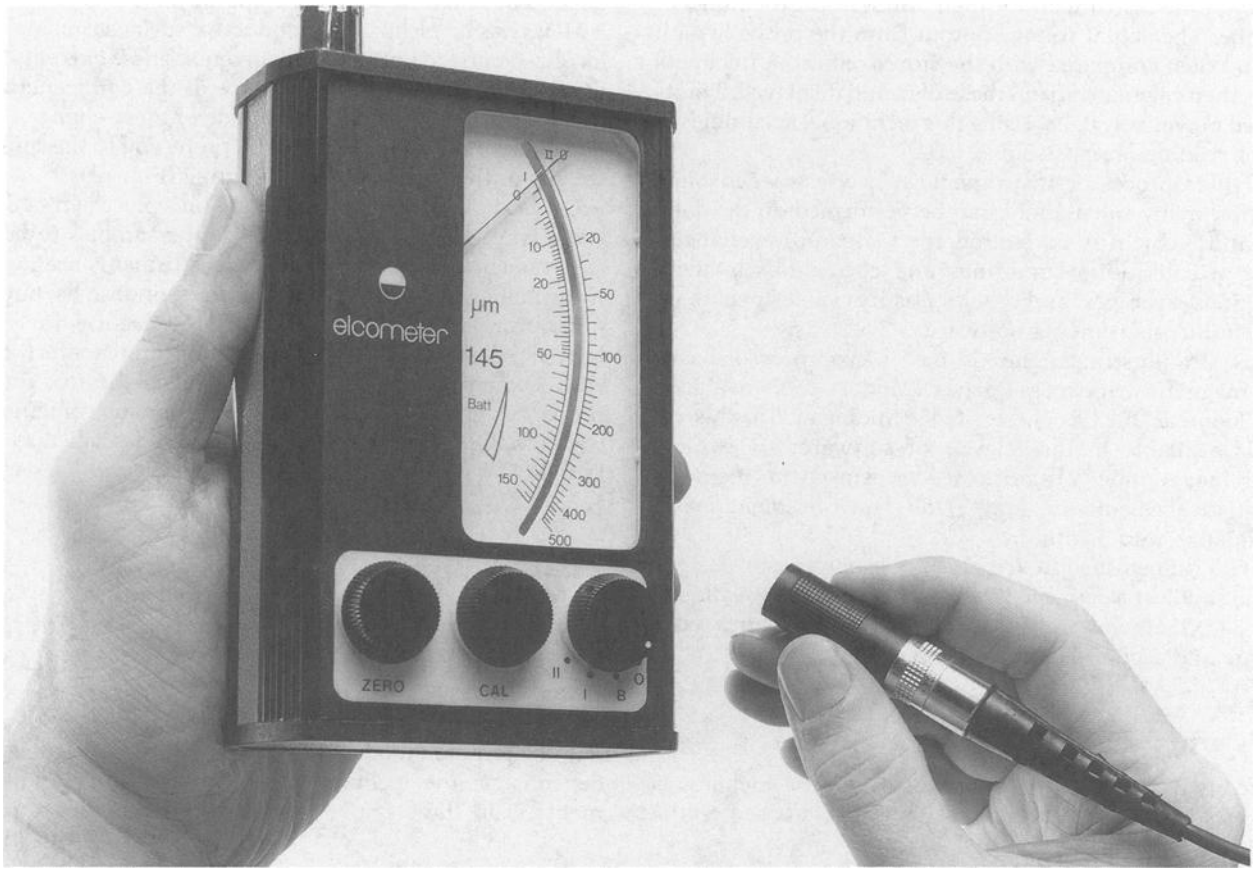

FIG. 14–Analogue electromagnetic thickness gage 145.

FIG. 15–Digital electromagnetic thickness gage 245.

memory of the instrument for many values over the range of the probe. The actual voltage output from the probe is digitized and then compared with the stored values. A thickness value is then calculated from these data and displayed. This is achieved in typically 0.3 s. Using this technique, accuracies of ±1% of reading are possible.

As a microprocessor instrument is in effect a dedicated computer, many calculations can be performed on the data, and features such as correction for temperature changes, storage of calibration conditions and corrections to these calibrations, averages, and other statistical values can be included in the instrument's software.

Figure 16 illustrates one of the microprocessor-based electromagnetic thickness gages Model 256, available from Elcometer Inc., Rochester Hills, Michigan. This instrument is available in three levels of software: (1) *basic*—measurements only; (2) *statistical*—measurement, memory, and statistical calculation; and (3) *top*—measurement, memory, statistics, and printout.

Figure 17 illustrates the trends in microprocessor designs with the smallest electronic coating thickness gage available, Model 345, Launched in October 1991, the unit supersedes analogue and digital designs at a lower cost.

Eddy Current Thickness Gages

The eddy current method for measuring film thickness is applied to coatings on nonferrous metals. It is based on the effect that a high-frequency alternating field (3 000 000 Hz or 3 MHz) has an electrically conductive surface causing highly localized current flow or eddy currents. These currents generate their own magnetic impedance of the coil, generating a high-frequency field. The magnitude of these changes is proportional to the distance from the probe coil to the substrate, that is, to the thickness of the coating (Fig. 18).

Calibration by adjustment to zero on a piece of metal of the same type, shape, and thickness as the samples to be measured is vital to ensure accuracy. Instruments are available using analogue, digital, or microprocessor designs, but many microprocessor instruments offer the facility for a dual ferrous (F) electromagnetic induction and nonferrous (N) eddy current principle instrument using the two different probe designs such as the eddy current instruments illustrated in Fig. 19. This type of gage is also described as ASTM D 1400.

EFFECTS OF SURFACE FINISH, CURVATURE, AND SUBSTRATE COMPOSITION ON ELECTROMAGNETIC AND EDDY CURRENT MEASUREMENTS

The accuracy of coating thickness measurements carried out using the methods described in the last two subsections depends on the technique used in calibrating the instruments. The three major influences on the calibration are

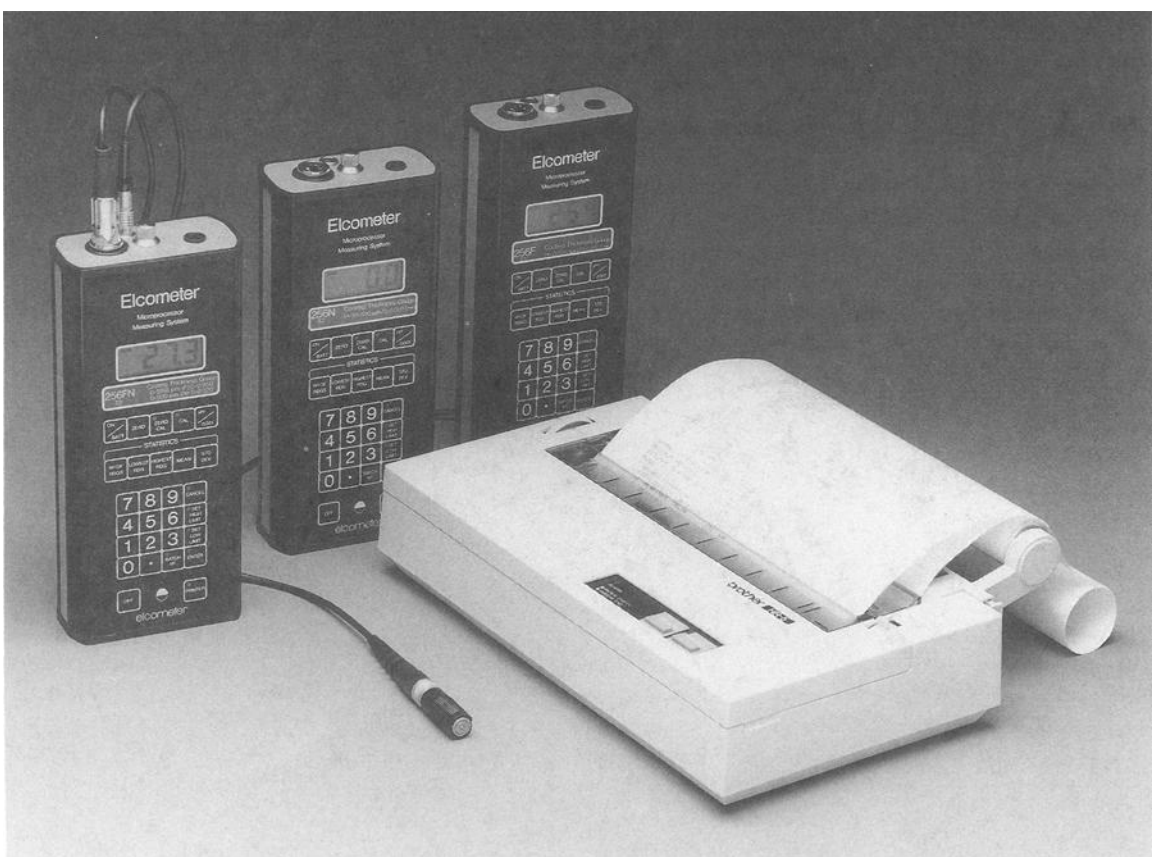

FIG. 16–Microprocessor electromagnetic thickness gage 256.

FIG. 17–Smallest microprocessor electromagnetic thickness gage 345.

surface finish, curvature, and shape of the substrate composition.

Surface Finish

A variety of surface finishes are to be found on metal to which a protective or decorative coating is to be applied. In some cases the coatings used require an anchor pattern of profile depth which forms a part of the specification. Comparators such as the Keane-Tator Surface Profile Comparator or the International Standards Organization ISO 8503 are used to determine the surface finish after shot or grit blasting. Also Testex Tape and the Elcometer Surface Profile Gage can be used to measure peak to valley heights of profiles. These instruments are shown in Fig. 20 along with the photographic standards for cleanliness ASTM Pictorial Surface Preparation Standards for Painting Steel Surfaces D 2200-1989 and SSPC-VIS1.

Surface finish also influences calibration as the quantity of metal directly beneath the probe is reduced by the effects of shot and grit blasting as the probe tip sits on the highest peaks. This has the effect of increasing the value of thickness indicated using a gage calibrated on a smooth surface by as much as 1.5 mils (35 μm) at 4 mils (100 μm) coating thickness for the highest values of profile.

It is possible to use a rough surface calibration technique to eliminate this error and make the instrument read the correct value of coating thickness over the peaks by using the statistical power of the microprocessor type gages to calibrate on the profile. This is achieved by using a thin foil 1.0 mil (25 μm) over the profile to set the lower calibration point and a thicker foil 5.0 mils (125 μm) or 10.0 mils (250 μm) to set the upper value over the profile. The instrument will then indicate the thickness over the peaks for the coating between the values of foil chosen.

This method is most accurate and reproducible when 15 to 20 readings are taken on each calibration foil to establish a mean value and the mean value is then reset to the correct value of the foil. Trials have shown that the mean of 15 to 20 readings taken over an area of coating give a mean value within a few percent of the actual value over peaks determined by sectioning.

The method does not, however, take into account situations where access to the substrate is not possible for calibration purposes. In this case, the method described in SSPC PA2 where a correction factor is applied to readings taken using a smooth surface calibration in the instrument is more appropriate. In either case it is important to agree with the method before measurements start to avoid discrepancies in reporting.

Curvature

The shape and metal wall thickness can also influence the accuracy of the calibration. The degree to which a particular instrument is affected depends on the design of the probe. Many modern instruments exceed the limits identified in SSPC PA2 of 1 Nov. 1982.

The effect of shape is most evident when taking readings on an uncoated sample. With an instrument calibrated on a smooth piece of metal 0.125 in. (3.175 mm) thick, changes of more than 0.2 mil (5 μm) in the reading at zero will be seen on curves with a radius below 0.12 in. (3 mm) convex or 0.96 in. (25 mm) concave on a typical electromagnetic induction probe. Values will vary between manufacturers and from different probe types.

This error can also be eliminated by calibration on a shape closely representing the specimen to be tested. However, it should be noted that once below the values of curvature indicated in the manufacturer's literature, changes in curvature have a significant effect on calibration, i.e., the calibration on a shape will not be applicable to another shape.

Substrate Composition

In the case of electromagnetic induction probes, most are insensitive to the majority of steel specifications in general engineering use. However, when high-carbon steels are coated, the carbon content sufficiently alters the magnetic properties of the steel to cause the normal calibration curve applied within the instruments to be in error with respect to linearity. Thus, an instrument calibrated at zero and say 5 mils (125 μm) may have an error at 2 mils (50 μm) of more than 0.2 mil (50 μm) or 10%. A similar effect can be seen with some cast irons.

This error can be overcome by calibrating as for the rough surface described in the section earlier in this chapter entitled **Surface Finish.** For best accuracy, choose a foil just below the expected coating thickness value for the lower calibration

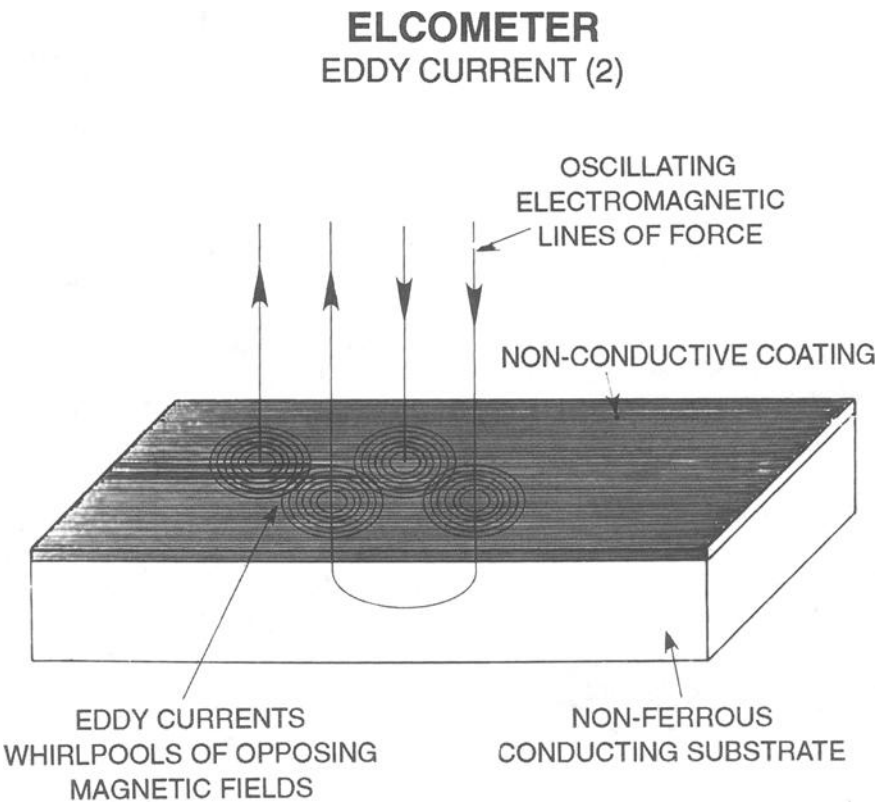

FIG. 18–Eddy current principle.

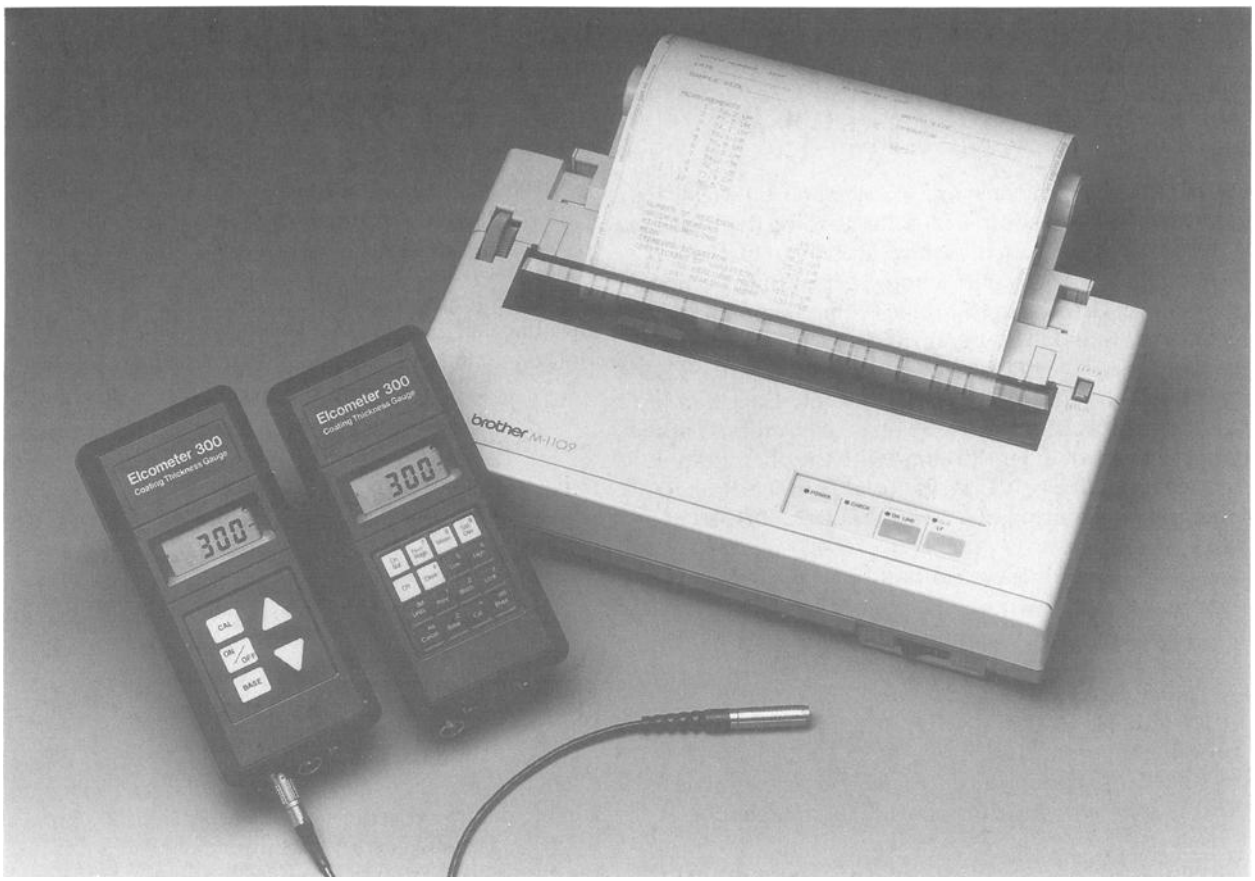

FIG. 19–Microprocessor eddy current gage model 300.

FIG. 20–Surface profile instruments (group) with model numbers as brochure.

points and a value well above the expected coating thickness value for the upper calibration point.

When coatings applied to nonferrous metals are being measured using eddy current techniques, the composition of the substrate and its effect on electrical conductivity are the important factors with respect to calibration. Materials such as aluminum and copper have very similar characteristics and similar calibration values. However, zinc, brass, and other nonferrous metals and alloys have different characteristics, and calibration on an uncoated sample is essential. Differences of up to 2 mils (50 μm) can be seen between "zero" with an aluminum calibration and zero on a brass component.

TABLE 4—X-ray fluorescence can be used for these applications.

Coating	Substrate
Chromium	Steel, copper
Cadmium	Steel, copper
Copper	Steel, zinc, brass
Nickel	Steel, copper, Kovar, aluminum, Alloy 42, inconel
Nickel-phosphorous	Steel, copper, Kovar, aluminum, Alloy 42
Zinc	Steel, copper, brass
Zinc-nickel	Steel
Gold	Nickel, aluminum, Kovar
Rhodium	Nickel, gold
Palladium	Nickel
Silver	Steel, copper, Kovar
Tin	Steel, copper, Kovar, aluminum
Titanium nitride	Steel
Ferrous oxide	Aluminum, plastic

STATISTICS IN FILM THICKNESS MEASUREMENT

As many random variations can be expected in a coating process, it is appropriate to classify the thickness of the coating using a statistical analysis. In fact, many national specifications utilize a statistical approach in recognition of these variations, e.g., SSPC PA2.

The sources of these variations are many, and only a few examples can be cited here—operator error in taking the measurement, recording error, variation due to surface or curvature or composition, local variation in substrate due to local heat treatment or due to forming or working the metal, inclusions in the metal or in the coating, etc.

The influence of these factors can be greatly reduced by taking a statistically significant number of readings for each area of the coating to be tested. This group of readings can then be summarized using mean and either standard deviation or range to show the average and the spread of readings about the average.

A statistically significant number of readings would be 20 to 50; however, if the process is under statistical control as defined, five readings in each group or subgroup is sufficient.

Many of the microprocessor-based coating thickness instruments are capable of calculating and recording mean

values ($\bar{x}$), standard deviation (σ), and highest and lowest values (range) within a batch of readings.

It is important to establish the method of evaluating the information before embarking on an evaluation of a coating system so that the correct disciplines are applied to collecting the data and evaluating it for further decisions.

X-RAY FLUORESCENCE (XRF)

Over recent years, developments in performance and reductions in cost have pushed X-ray fluorescence to center stage, particularly for metal-on-metal applications and ever smaller parts. Beta-ray backscatter (BBS) techniques had been widely used to measure plated coatings; however, limitations in performance—e.g., a minimum of 20% difference in atomic number between the coating and the substrate is required—mean that while gold over nickel, copper, or Kovar can be measured, nickel over copper or Kovar cannot be measured using BBS techniques. Other disadvantages exist, such as limits in the aperture/component geometry, and measurement times have led to the further development of XRF techniques and technology.

Principle of XRF Measurement [6]

If sufficient light energy collides with an electron, it is possible for the electron to be driven out of its atomic orbit, a process known as the photoelectric effect. An atom with an electron removed from its orbit is unstable, so to restore equilibrium, an electron from a higher shell must drop into the vacant orbit. This transition causes an emission of energy in the form of a light wave or photon.

When the inner shell electrons are ejected from an atom, the emitted photon has high energy, and they fall into the region of the electromatic spectrum called X-rays. X-rays have characteristic energy levels determined by the element which is emitting and can therefore be used to identify the elements in a sample.

In XRF instruments an X-ray source or tube is used to produce photon emissions as they have an energy distribution capable of fluorescing all elements commonly used in plating. The X-ray beam can be accurately illuminated to provide a small focal spot and high-intensity energy suitable for noncontact measurement of complex layers on small components. The characteristic X-rays emitted by the target materials are detected using a gas-filled "proportional counter" in which the passage of the X-ray ionizes the gas and produces a pulse of electrical charge proportional to the energy of the X-ray.

The XRF instruments' electronics convert the charge pulse into a digital signal that can be interpreted as thickness or analyzed for composition and produce the measurement information by comparison with standards of known thickness. XRF instruments have developed with optical alignment systems and motor-driven sample stages to position the sample and computerized analytical equipment to store calibration data to calculate and present data to the user in a suitable format. Table 4 shows some of the applications which can be successfully measured using XRF.

REFERENCES

[1] New Jersey Zinc Co., "Leaves from a Paint Research Note Book," No. 1, 1937, p. 33.

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Drying Time

by Thomas J. Sliva[1]

THE PROCESS OF DRYING INVOLVES several physical and/or chemical changes, such as solvent evaporation, oxidation, and polymerization, all of which are time dependent. The various stages of drying that occur in organic films may be subjective, difficult to measure reproducibly, and are influenced by many factors such as film thickness, substrate, temperature, humidity, light, and air circulation. Therefore, it is essential that most of these variables must be minimized in order to make drying time determinations more quantitative.

PREPARATION OF SPECIMENS

Substrate Preparation

It is essential that the substrate to be used and the applied wet film thickness be agreed upon in advance, preferably to conform to the intended use of the coating. Flat glass panels are typically the substrate of choice. Ground and polished glass plates are more suitable for low-viscosity coatings that may tend to crawl. All panels must be thoroughly cleaned, dried, and placed in a horizontal position on a level surface.

Application

The test coating should be filtered to remove any dirt or contamination. Test films are typically prepared, in duplicate, using a drawdown or doctor blade adjusted to obtain a uniform film thickness. Films should be drawn down at a uniform rate of application to avoid drag on the coating. It is recommended that all test films should be prepared and tested by one operator properly skilled in the method to be used and that a control (known) coating be run alongside the test coating. All testing should be done within an area, any point of which is not less than ½ in. (15 mm) from the edge of the test film.

Table 1 can be used as a general guide for film application when nothing more specific is agreed upon between the purchaser and seller. The dry film thicknesses shown in Table 1 are suggested.

Other methods of application, such as spraying, dipping, or flood coat, may be used provided the film thickness obtained is consistent with that recommended under actual usage. Other substrates, such as metal, may be used provided they are smooth and flat.

[1]Assistant technical director, DL Laboratories, 116 East 16th St., New York, NY 10003.

ENVIRONMENT

When determining drying time, a controlled environment is essential. Variations in temperature, relative humidity, and circulation of air and light will have an effect on the drying time of a coating. The typical standard environment used for determining the drying time of air dry coatings is a temperature of 73.4° ± 3.6°F (23° ± 2°C) and a relative humidity of 50 ± 5% under diffuse daylight (about 25 fc).

Relative humidity should be strictly controlled for moisture-cure and two-package urethane coatings since their cure is greatly affected by the existing relative humidity. The effect of variation in temperature was discussed by Algeo and Jones [*1*], who observed a difference of 4 h for a particular paint dried at 73 and 77°F (22.7 and 25°C), both at 50% relative humidity.

All testing should be conducted in a well-ventilated room free from direct drafts and dust. Airflow is important in determining drying time. For films that dry by oxidation, the rate of drying is a function of the concentration of oxygen at the interface. Since oxygen can reach the surface only by diffusion, the rate of drying is a function of the thickness of the stationary air layer. For films that dry by solvent evaporation, the continuous removal of solvent-laden air hastens drying.

TEST METHODS

ASTM D 1640: Test Methods for Drying, Curing, or Film Formation of Organic Coatings at Room Temperature

Method D 1640 is the most commonly used method to determine the various stages and rates of film formation in the drying of organic coatings normally used under conditions of ambient room temperature. The method describes eight stages of the drying process:

1. *Set-To-Touch Time*

   The test film is lightly touched with the tip of a clean finger, and the fingertip is immediately placed against a piece of clean, clear glass to determine when the film does not adhere to the finger or transfer to the glass.

2. *Dust-Free Time*

   This test is generally performed by either of two methods that determine when dust or cotton fibers lightly dropped

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TABLE 1—Recommended film thickness of materials to be tested.

Material	Dry Film Thickness, mils
Oil paints	1.8 ± 0.2
Enamels	1.0 ± 0.1
Drying oils	1.0 ± 0.1
Water-based paints	1.0 ± 0.1
Varnishes	0.85 ± 0.1
Lacquers, resins solutions	0.5 ± 0.1

on the test film can be removed by blowing over the test film.

a. *Cotton Fiber Test Method*

Individual absorbent cotton fibers are dropped from a height of 1 in. (25 mm). The film is considered to be dust free when the cotton fibers can be lightly blown off the test film.

3. *Tack-Free Time*

The test film is considered to be tack free when no stickiness is observed under moderate pressure. This can be measured by either of two methods:

a. *Paper Test Method*

A special paper (K-4 Power Cable Paper) [*3*] is placed on the test film under a weight of 2 psi (13.8 kPa). After 5 s, the weight is removed and the test film inverted. If the paper drops off within 10 s, the film is considered tack-free.

A variation of the above method is used to test the tack-free time of insulating varnishes. The varnish is considered tack free when the paper is placed on the test film under a weight of 1 lb (450 g) for 1 min and tested as above.

b. *Tack Tester*

This is a mechanical device which consists of a strip of metal 1 in. (25 mm) wide, 3 in. (75 mm) long, and 0.016 to 0.018 in. (0.41 to 0.46 mm) in thickness. It is bent to form a base 1 in. (25 mm) square and a vertical length 1 by 2 in. (25 by 50 mm) angled at 135°. The bottom of the base of the tester is covered with aluminum foil [*4*] (Fig. 1). A 300-g weight is placed on the center of the base and allowed to set for 5 s. The test film is tack free when the tester tips over immediately after the weight is removed. Occasionally, tack-free time may be longer than dry-hard or dry-through time due to the inclusion of external plasticizers in the coating.

4. *Dry-To-Touch Time*

The test film is considered dry-to-touch when no mark is left when the film is touched by a finger. The following variations are used:

a. *Drying Oils*—The film is considered dry-to-touch when it does not rub up appreciably when a finger is rubbed lightly across the surface.

b. Lacquers (and Sealers)—The film is considered dry-to-touch when no pronounced marks are left by a finger touching the film. Sealers are generally tested on wood or other porous substrates.

5. *Dry-Hard Time*

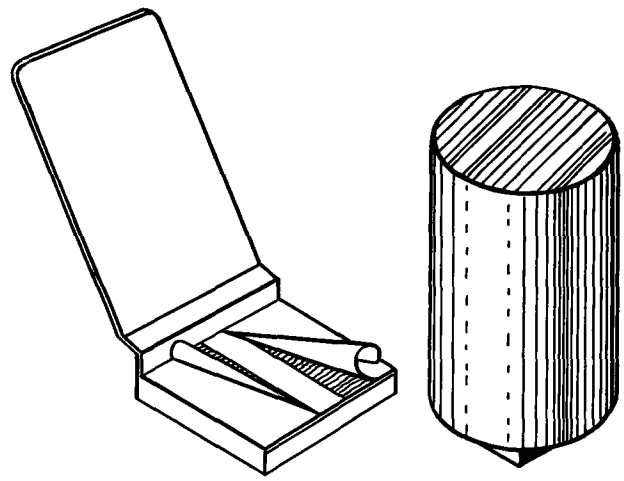


FIG. 1–Zapon Tack Tester. The base of the tester is padded and wrapped with aluminum foil. The weight, at right, is set on the base for a definite interval. After the weight is removed, the time required for the tester to tip over is the measure of tack.

The test film is considered dry-hard after maximum downward thumb pressure (without twisting) applied to the test film leaves no mark when the contacted area is lightly polished with a soft cloth.

6. *Dry-Through (Dry-To-Handle) Time*

The test panel is placed in a horizontal position at such a height than when a thumb is placed on the film, the arm of the operator is in a vertical line from the wrist to the shoulder. The operator bears down on the film with the thumb, exerting moderate pressure and at the same time twisting the thumb through an angle of 90°. The test film is considered dry through when the film is not distorted by bearing down with moderate thumb pressure and twisting 90°.

7. *Dry-To-Recoat Time*

The test film meets this requirement when a second coat can be applied without causing any film irregularities, e.g., lifting, wrinkling.

8. *Print-Free Time*

The test film meets this requirement when imprinting fabric under a pressure of ½ or 1 lb/in.^{2} (3.5 or 7.0 kPa) shows the coating to be print free. This procedure is similar to ASTM D 2091: Test Method for Print Resistance of Lacquers.

An indication of the accuracy of these methods is the precision statement developed in ASTM D 1640 in which duplicate determinations within a laboratory should agree within ±10% [*5*].

Federal Test Method Standard 141C, Method 4061.2: Drying Time

This method is similar to ASTM D 1640. It includes essentially the above stages of drying with the exception of dry-to-

touch. However, it includes a test for free-from-after-tack. This test is applicable to coatings where tackiness persists beyond, or reappears at, the through-dry stage. It is similar to the Paper Test Method, discussed earlier in this chapter, except that a 2.8-kg (6.2-lb) weight is used.

ISO Standard 9117: Paints and Varnishes—Determination of Through-Dry State and Through-Dry Time—Method of Test

This standard describes a method for determining under standard conditions whether a single coat or a multi-coat system of paint or related material has, after a specified drying period, reached the through-dry state, i.e., a pass/fail test. The test procedure may also be used to determine the time taken to achieve that state.

1. *Through-Dry State*

   This state defines the condition of a film in which it is dry throughout its thickness as opposed to that condition in which the surface of the film is dry but the bulk of the coating is still mobile. A single coating or a multi-coat system of paint or varnish is considered to be through-dry when a specified gauze attached to a plunger is placed on the test film under specified pressure (1500 g) for 10 s, after which time the plunger head is turned through an angle of 90° over a period of 2 s and removed (Fig. 2). If no damage or markings are noted on the test panel, the film is said to have achieved "through-dry state."

2. *Through-Dry Time*

   This is the period of time between application of a coating to a prepared test panel and the time to achieve the "through-dry state" as outlined above.

British Standard B.S. 3900: Methods of Test for Paints

Parts C-1 thru C-4 of British Standard B.S. 3900 describe drying tests for determining the wet edge time, surface drying, hard-drying, and freedom from residual tack tests. Part C-8 describes a test for determining print-free state or time.

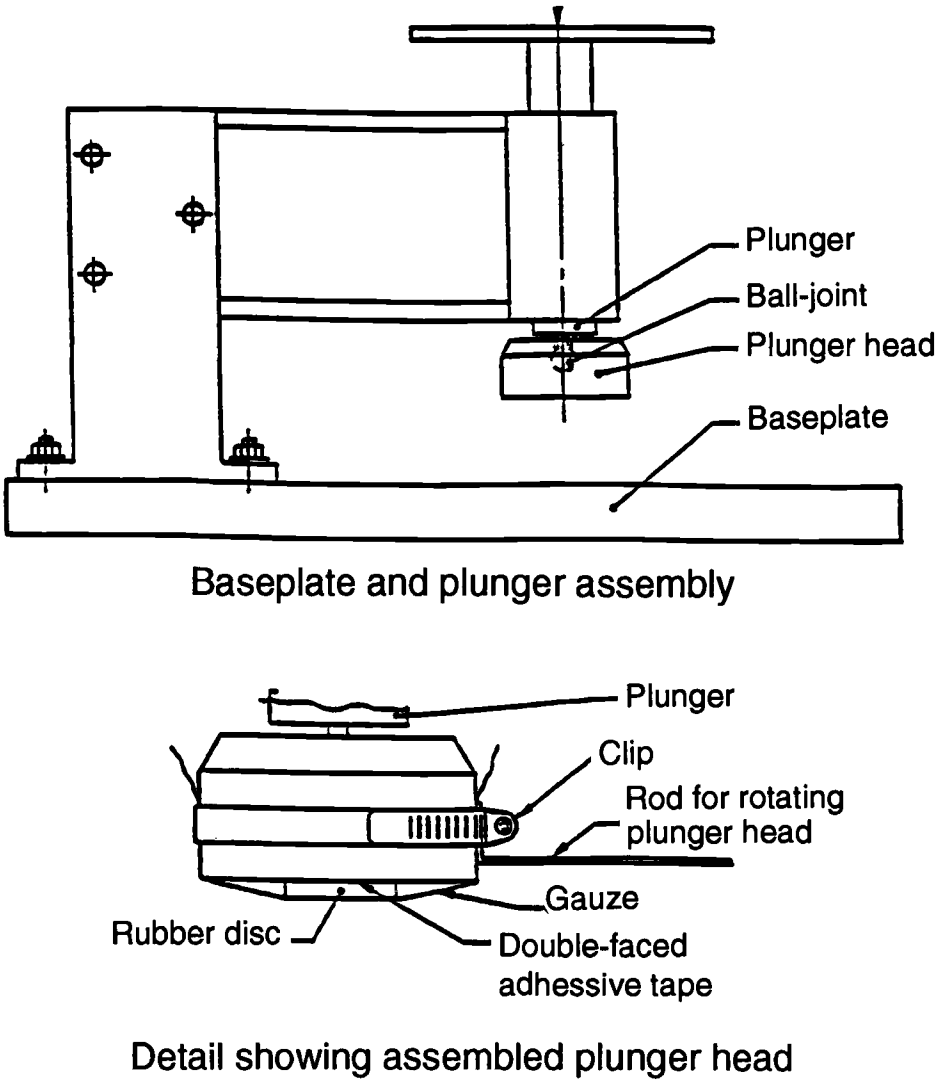


FIG. 2–Through-Dry Tester.

1. *Wet Edge Time (BS3900, C1)*

   This procedure is used for determining whether the edge of a film of paint remains "alive" after a specified period of drying. Following a touch-up coat over the film after the specified drying period, the area is evaluated for lack of film continuity, absence of leveling, or variation in color or sheen.

2. *Surface Drying (BS3900, C2)*

   This procedure is used to determine the time after which a coating is applied and when approximately 0.5 g of the ballotini (small transparent solid glass spheres) can be poured onto the surface of the film from a height of between 50 and 150 mm and lightly brushed away without damaging the surface.

3. *Hard-Drying Time (BS3900, C3)*

   A rubber-faced plunger is covered with cotton twill, rough side outwards, and then loaded to a toal weight of 1.8 kg (4 lb). The rotating plunger drops into the panel and makes a three-quarter turn while in contact. The paint film is dry-hard when no damage is observed (Fig. 3).

4. *Freedom from Residual Tack (BS3900, C4)*

   After a specified drying period, a paper-backed gold leaf is placed on the test panel and covered with a microscope slide and an 800-g weight. After 10 s, the weight and slide are removed and the panel is held vertically and lightly tapped to detach the gold leaf. The surface of the paint film is examined for adhesion of gold leaf.

5. *Print-Free (BS3900, C8)*

   The state of a coating or varnish when gauze of a specified grade, under specified force and after a specified time, does not leave an imprint on the surface of a coating.

DIN 53 150: Determination of Drying Time of Paints

Drying time is determined in this method by the adherence or nonadherence of sand or paper to the film under various loadings. Stage 1 is determined with sand (0.16 to 0.315 mm) or glass beads (ballotini). The sand is allowed to remain on the film for 10 s. The remaining stages are determined using disks of typewriter paper (22 mm in diameter and weighing about 60 g/m^2) and various loads ranging from 5 to 5000 g/cm^2. Interposed between the load and the test disk is a soft rubber cushion. The load remains on the disks for 60 s. The criteria for the seven stages are as follows:

1. Sand easily removed with a soft brush.
2. Disk under load of 5 g/cm^2 does not adhere.
3. Disk under load of 50 g/cm^2 does not adhere.
4. Disk under load of 500 g/cm^2 does not adhere, but film is temporarily marred.
5. Disk under load of 500 g/cm^2 does not adhere, but film is not marred.
6. Disk under load of 5000 g/cm^2 does not adhere, but film is temporarily marred.
7. Disk under load of 5000 g/cm^2 does not adhere, but film is not marred.

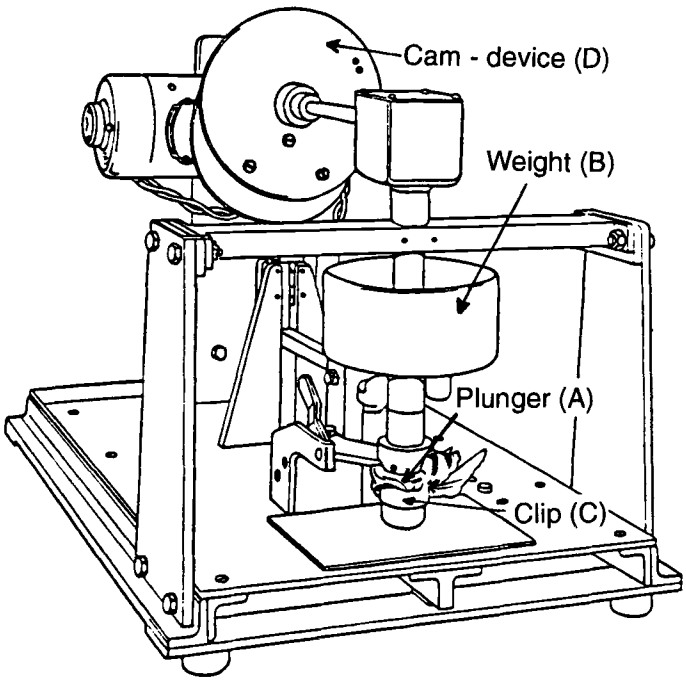


FIG. 3–Hard-drying time apparatus: Assembly.

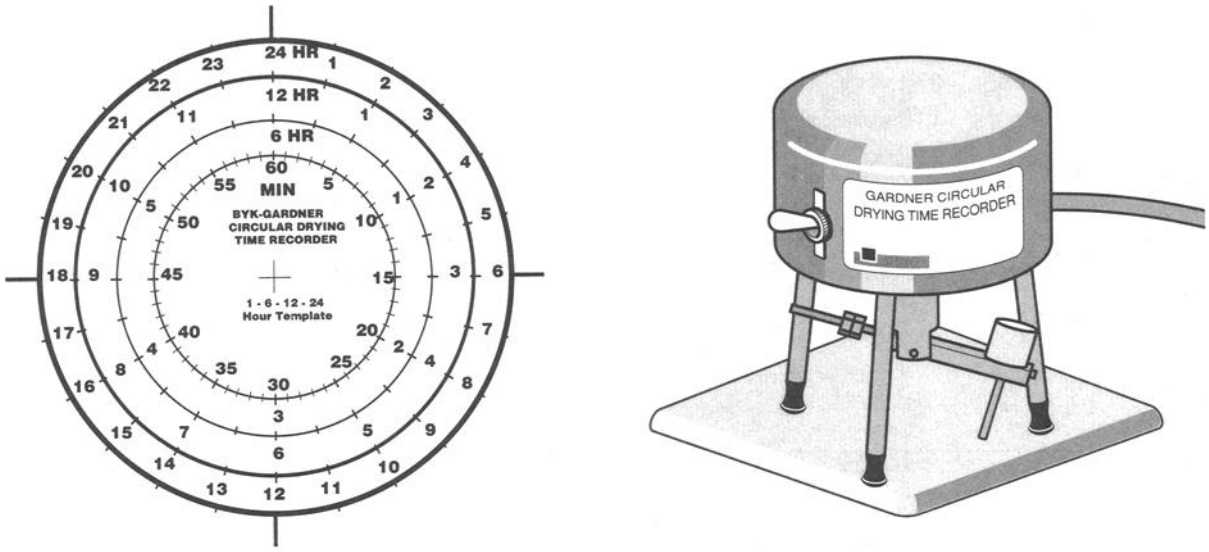


FIG. 4–Circular drying time recorder. (Courtesy of Byk-Gardner.)

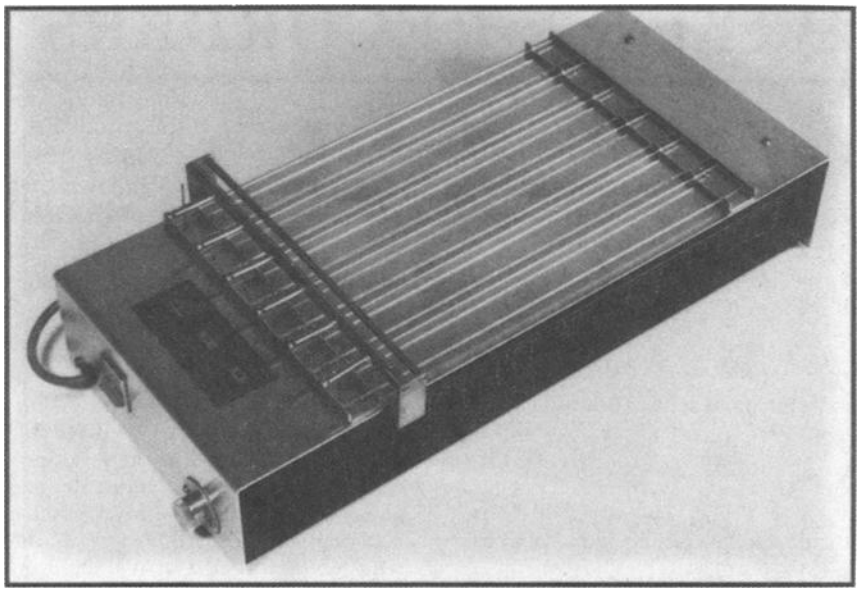


FIG. 5–Straight line recorder. (Courtesy of Byk-Gardner.)

MECHANICAL DEVICES

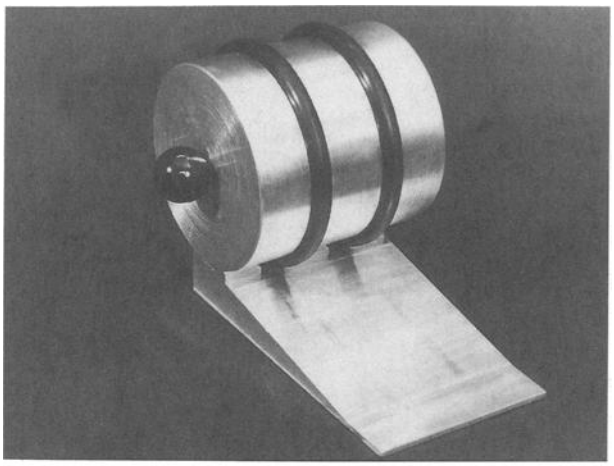
In an attempt to improve the accuracy and reproducibility of the drying time test procedure, various mechanical devices have been developed. The following sections outline these devices and the procedures used in determining drying characteristics.

Circular Drying-Time Recorder

The device consists of a synchronous motor in a metal case resting on a rubber-tipped tripod and rotating a vertical shaft. A pivotal arm assembly is attached to the shaft, operating a vertical stylus with a Teflon sphere that does not stick to the drying film [6]. Under a 12-g load, the stylus scribes an arc in the drying film. Motor speeds are available to cover drying times of 1, 6, 12 and 24 h (Fig. 4).

A transparent template with time increments can be placed over the dried coating at the end of the test. The appropriate time circle can then be used to determine the dry time. During the early stages of drying, the coating tends to flow back into the wake of the stylus. When the tendency of the flow has ceased, the film may be considered set. As the drying process continues, a skin will form. Visually, this part of the film formation is seen when the stylus begins to tear the surface of the film. The film may be considered surface dry or dust free when the skin is no longer ruptured by the stylus. It is considered through dry when the stylus rides above the film.

Circular drying time devices have been developed for use when determining the drying time of bake finishes that cure



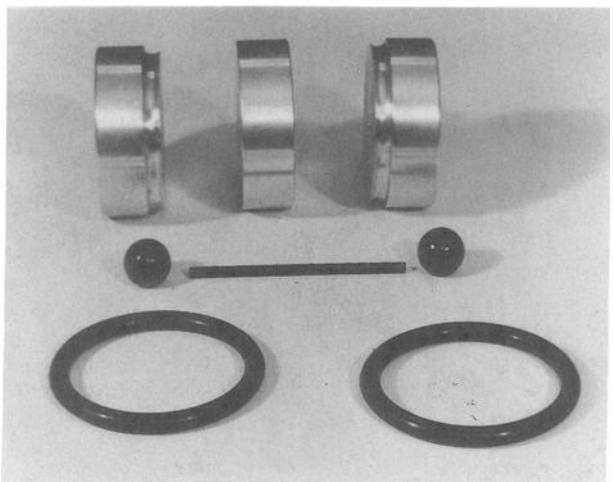


FIG. 6–No pick-up time traffic paint roller. (Courtesy of Byk-Gardner.)

at elevated temperatures [up to 500°F (260°C)]. The compactness of the instrument allows the user to place it in an oven at a specified temperature.

Straight Line Drying Time Recorder

This device consists of multiple needles being drawn over multiple (up to six) parallel coated glass strips [7]. Its speed can be varied to cover drying periods of 6, 12 and 24 h (Fig. 5). It defines the following stages in the drying process:

1. The first stage is a pear-shaped depression corresponding to the time it takes for the solvent to evaporate.
2. The second stage is the cutting of a continuous track corresponding to a sol-gel transition.
3. The third stage is an interrupted track corresponding to the surface dry time.
4. In the fourth stage, the needle no longer penetrates the film, indicating the final drying time.

Five-gram brass weights may be added to apply greater pressure on the needles and thus record through drying. The instrument has also been found useful in evaluating gel time of many two-component surface coatings.

I.C.I. Drying Time Recorder

This instrument consists of a metal box platform which will accommodate flat panels, usually made of glass. A gantry moves between and parallel to the long dimension of the flat panels [8]. This gantry will carry up to three detachable devices for each panel. These include a flock dispenser, a sand hopper, a bandage roller, and a ball-pointed needle. These can be used in any combination to test up to six coatings, three on each panel.

The different stages in drying which can be measured, depending on the device used, are dust free, surface dry, and dry through.

NO PICK-UP TIME TRAFFIC PAINT ROLLER

This device is described in ASTM Standard D 711: Test Method for No-Pick-Up Time of Traffic Paint.

The apparatus consists of a steel cylinder weighing 11 lb, 14 oz (5385 g) with two O-rings [6]. It is rolled along a drying film of traffic paint which has been applied on a glass plate. The paint is dry when no paint adheres to the O-rings (Fig. 6).

REFERENCES

[1] Algeo, W. J. and Jones, P. A., "Factors Influencing the Accurate Measurement of Drying Rates of Protective Coatings," *Journal of Paint Technology*, JPTYA, Vol. 41, 1969, p. 235.

[2] The dust-free tester was designed and built by Technical Subcommittee 37 of the New York Paint and Varnish Production Club and is described in "Investigation of Methods for Measuring Drying Time," *Official Digest, Federation of Paint and Varnish Production Clubs*, ODFPA, Vol. 20, November 1948, pp. 836–843. This paper also includes a study of the Zapon Tack Tester.

[3] Paper meeting this requirement may be obtained from Crocker Technical Papers, Inc., 431 Westminster St., Fitchburg, MA 01420, their Grade R 20-34.

[4] U.S. Patent 2,406,989, 3 Sept. 1946. It is known as the Zapon Tack Tester.

[5] See Prane, J. W., "A Latin Square Drying Time Study," *Paint Industry Magazine*. August 1961, for a study of precision of drying time measurements.

[6] Available from Byk-Gardner, Inc, Gardner Laboratory 2435 Linden Lane, Silver Spring, MD 20910 or Paul N. Gardner Co., Inc., 316 N. E. First Street, Pompano Beach, FL 33060.

[7] Available from T. J. Bell Inc., 1340 Home Avenue, Akron, Ohio 44310, as well as manufacturers listed in Ref 6.

[8] Available from Erickson GMBH & Co., KG, D-5870 Herner, Germany and Paul N. Gardner Co., Inc., 316 N.E. First Street, Pompano Beach, FL 33060.

Part 10: Optical Properties

40

Color and Light

by Fred W. Billmeyer, Jr.[1] *and Harry K. Hammond, III*[2]

BECAUSE COLOR IS A SIGNIFICANT FACTOR in the appearance of an object, it is an important characteristic of any paint. Appearance, of which color is a part, is one quality of a product that every customer can judge for himself. No matter how good the physical properties of a paint, if its color does not meet the expectation of the customer, the finished product will be rated as unsatisfactory.

Color, often thought to be a property of the paint itself, depends on three objective aspects: (1) the spectral composition of the light in which the paint is viewed, (2) the spectral reflectance of the paint, and (3) the spectral response of the eye of the observer. The subjective interpretation of the response to these aspects by the brain is also an essential part of color. Describing the color of a paint or other material requires consideration of all of these and not merely the spectral character of the material. The three objective aspects of color are considered in sections entitled **LIGHT SOURCE, REFLECTION AND TRANSMISSION**, and **THE EYE**. The sciences involved include chemistry, physics, physiology, and psychology. These are broad subjects, and only enough discussion is included to provide a background for understanding the development of test methods. Readers desiring to pursue these subjects in detail should consult an appropriate text [*1–6*].

TERMINOLOGY

To understand this chapter and to make the best use of it, the reader should be familiar with the terminology of appearance. The precise definition of terms is becoming increasingly important in today's world community. The paint terminology standard, ASTM Definitions of Terms Relating to Paint, Varnish, Lacquer, and Related Products (D 16), is the primary source of terms and definitions relating to paint, but it contains very few appearance terms. The reader should refer to ASTM Terminology of Appearance (E 284) for terms and definitions relating to color and other appearance attributes. All significant terms used in this section are defined in ASTM E 284.

An important international source of appearance terms is the *International Lighting Vocabulary* [*7*], published jointly by the International Commission on Illumination (CIE) and the International Electrotechnical Commission (IEC). However, this is structured from the viewpoint of illuminating engineering. It is less readily available and a much more costly document than ASTM E 284.

LIGHT SOURCES

Light is electromagnetic radiation weighted by the response of the normal human eye. It occupies a small portion of the electromagnetic spectrum between ultraviolet and infrared radiation. Its wavelength range is approximately 380 to 780 nm (Fig. 1).

Natural and Artificial Daylight

Despite modern dependence on interior illumination, daylight is still an important light source since most objects are at some time viewed in it. The spectral composition of daylight, however, is quite variable, depending upon the hour of day, the season of year, and the amount of cloud cover. One way of dealing with this variability is to use standard light sources and their spectral power distributions when making visual or instrumental color measurements and calculations (see later in this chapter under **CIE Standard Sources and Illuminants**).

Incandescent Sources

Other light sources must replace daylight when appropriate. For use in homes, incandescent lamplight is generally preferred because it imparts a soft, mellow effect similar to that of candlelight.

Fluorescent Sources

In stores and offices, fluorescent lamps can provide high levels of illumination with low power consumption and heat generation. The most commonly used fluorescent lamp, known as cool white, has a spectral distribution consisting of a relatively smooth curve throughout the visible spectrum. This arises from the fluorescent emission from a phosphor coated on the inside of the lamp tube. The fluorescence is excited by ultraviolet radiation from mercury vapor inside the tube. This lamp is, however, deficient in power in the red end of the visible spectrum. Modifications of it, known as deluxe and super-deluxe versions, have been designed to overcome this deficiency. Fluorescent lamps have also been

[1]Color consultant, 1294 Garner Avenue, Schenectady, NY 12309-5746.
[2]Consulting scientist, BYK-Gardner, Inc., 2435 Linden Lane, Silver Spring, MD 20910.

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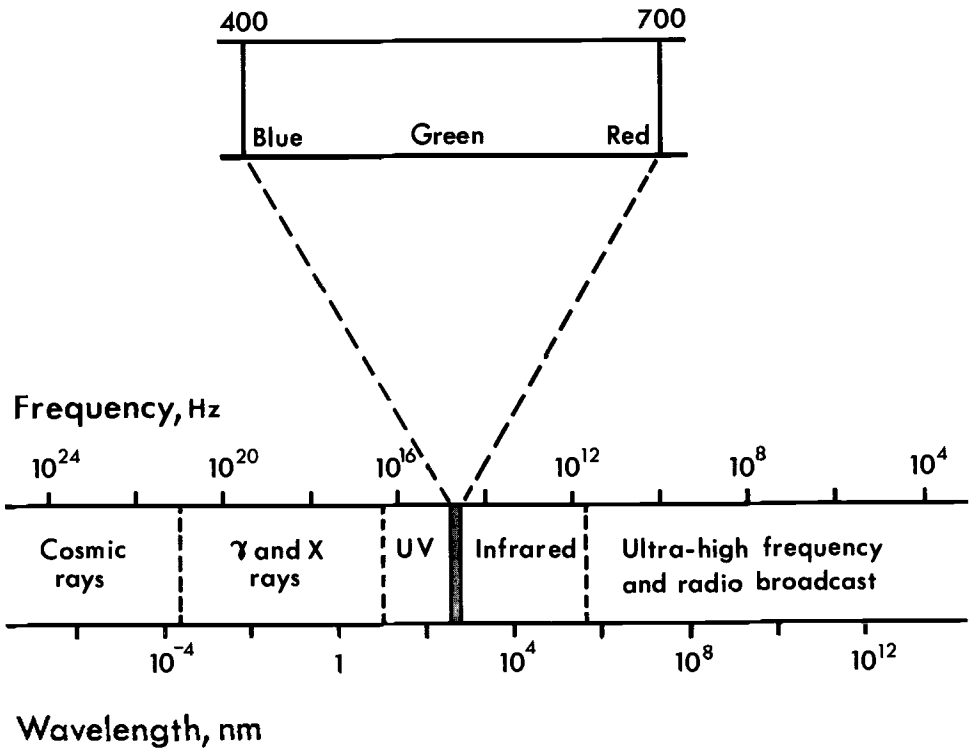

FIG. 1–Electromagnetic spectrum showing the relatively small portion that the visible spectrum occupies.

designed with phosphors emitting only in three rather narrow regions of the spectrum. When these three bands are selected to peak near 450, 530, and 610 nm, light is provided that is especially pleasing to the eye and energy efficient.

The color-balance and color-rendering properties among the various types of commercial fluorescent lamps can be vastly different one from another.

Other Sources

Other light sources have been developed for special purposes. They include arc lamps (sodium, mercury, neon, xenon), metal halide lamps, and high-intensity discharge (HID) lamps. None of these lamps has been adopted as standard for use in color measurement.

Color-Matching Booths

Because of the variation in spectral composition of different natural and artificial sources, it is essential that visual color matching be done under standardized illumination, such as that provided by a color-matching booth. This device allows the colorist to compare the colors of specimens under controlled and standardized illumination. Carefully manufactured and maintained light booths permit a colorist to make a visual match with confidence that the illumination duplicates that used at another time or place. However, the spectral power distribution of daylight illumination in color-matching booths is not the same as that of natural daylight.

REFLECTION AND TRANSMISSION

Opaque, Transparent, and Translucent Films

When light strikes an object, some of it may be reflected, some may be absorbed, and if the object is not opaque, some may be transmitted. The reflected light may be concentrated in a glossy, mirror-like reflection, scattered uniformly in all directions, or distributed between these two extremes, which are known as specular reflection and diffuse reflection, respectively. A highly polished metal can reflect as much as 99% of the incident light in the specular direction. A white powder, such as barium sulfate, scatters light uniformly in all directions, and it, too, can reflect as much as 99% of the incident light. Specular reflection is related to the visual perception of gloss; diffuse reflection is related to the visual perception of lightness and, when it is wavelength dependent, to that of color.

Transmission can also be diffuse or regular, depending on whether or not light is scattered in passing through a material. Specimens that both transmit and reflect light are called translucent.

A spectrophotometer is used to provide information on the spectrally selective character of a material. Figure 2 shows typical spectral reflectance curves of some paints. A trained colorist can obtain valuable information from such curves, but spectral data alone are unsatisfactory as a means for color identification.

Among the ASTM standards on reflectance and transmittance measurement [*8*], the most useful include ASTM Practice for Obtaining Spectrophotometric Data for Object-Color Evaluation (E 1164), ASTM Test Method for Reflectance Factor and Color by Spectrophotometry Using Hemispherical

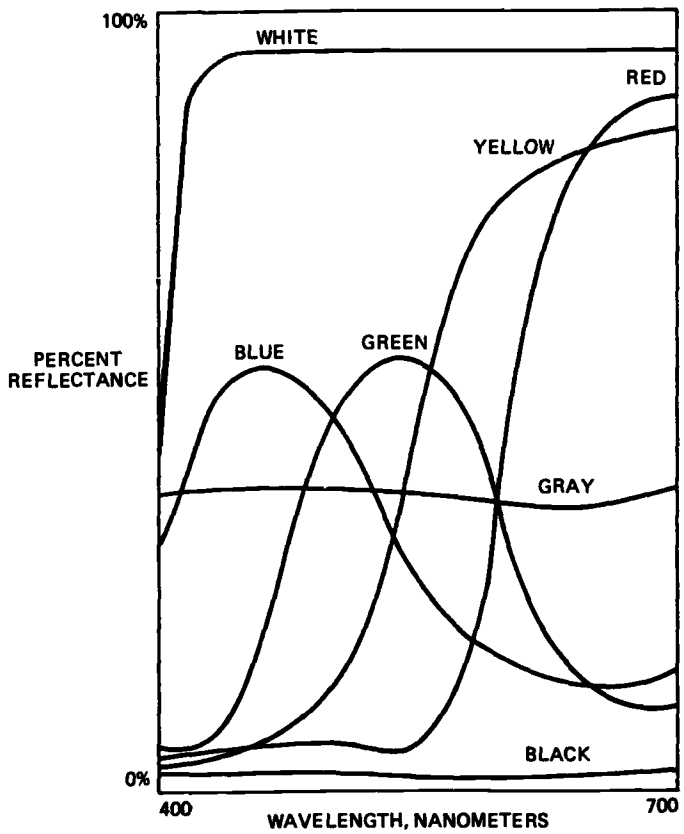

FIG. 2–Spectrophotometric curves typical of those measured on paint films. Note the sharp drop in the curve for rutile titanium dioxide (white) as the violet end of the spectrum is approached. The drop continues in the ultraviolet, where this pigment absorbs light strongly. (Based on Ref. 2.)

Geometry (E 1331), ASTM Test Method for Color and Color-Difference Measurement by Tristimulus (Filter) Colorimetry (E 1347), ASTM Test Method for Transmittance and Color by Spectrophotometry Using Hemispherical Geometry (E 1348), and ASTM Test Method for Reflectance Factor and Color by Spectrophotometry Using Bidirectional Geometry (E 1349).[3]

Ultraviolet and Infrared Spectral Regions

Ultraviolet and infrared radiation can have important effects on paint. Ultraviolet radiation, with wavelengths shorter than 380 nm, is the principal stimulus of fluorescence of certain pigments, is an aid to identification and analytical determination of certain ingredients of paint, and may promote decomposition of pigments or binders. Colorless pigments absorbing in the ultraviolet region can impart protection against such decomposition. Rutile titanium dioxide absorbs in the ultraviolet, as its spectral curve shows (see Fig. 2).

[3]As noted in ASTM E 284, in the Discussion under *reflectance*, "The term *reflectance* is often used in a general sense or as an abbreviation for *reflectance factor*. . . ." This simplifying convention is used in this chapter, as it is in many textbooks. The reader should refer to ASTM E 284 for the definitions of *reflectance, transmittance,* and *radiance,* and the corresponding factors. Note that commercial instruments measure *reflectance factor,* not *reflectance.*

Infrared radiation, with wavelengths longer than 780 nm, is associated with heat transfer. It is widely used for the identification and analysis of chemical compounds. The near-infrared region, with wavelengths from 780 to about 10 000 nm, is important for camouflage detection. Most paint pigments do not absorb radiation in this region, but some inorganic pigments reflect visible light and absorb radiation in the near-infrared.

Fluorescence

Some materials have the property of fluorescing when irradiated by ultraviolet or short-wavelength visible radiation. They emit radiation at longer wavelengths in the visible range or even in the near-infrared. The effect of fluorescence is to increase the apparent reflectance since the eye responds to the sum of the fluoresced and the reflected energy. This sum may even exceed the amount of light reflected by an ideal white material at the wavelengths of maximum fluorescent emission. Many fluorescent pigments have relatively poor lightfastness in outdoor applications.

Most modern colorimeters and spectrophotometers are designed to evaluate properly the colors of fluorescent materials, although many do not have light sources adequately simulating the ultraviolet content of natural daylight. In such a case the instrument will not produce the same amount of fluorescence as would daylight.

Two ASTM standards apply to the measurement of fluorescence. ASTM Test Method for Identifying Fluorescence in Object-Color Specimens by Spectrophotometry (E 1247) provides two instrumental methods to supplement simple visual examination of the specimen under ultraviolet light to detect the presence of fluorescence. ASTM Practice for Color Measurement of Fluorescent Materials (E 991) specifies the instrument geometry required for the measurement and shows how to assess the performance of daylight-simulating instrument light sources.

Retroreflection

Retroreflection is defined in ASTM E 284 as "reflection in which the reflected rays are preferentially returned in directions close to the opposite of the direction of the incident rays. . . ." It is important in paints and coatings used for signs viewed at night, pavement and pedestrian markings, and other safety devices. The measurement of retroreflection requires special instrumentation and special test methods for the determination of daytime and nighttime colors of retroreflecting materials. Among the ASTM standards dealing with this subject are: ASTM Practice for Describing Retroreflection (E 808), ASTM Practice for Measuring Photometric Characteristics of Retroreflectors (E 809), ASTM Practice for Measuring Colorimetric Characteristics of Retroreflectors under Nighttime Conditions (E 811), ASTM Test Method for Coefficient of Retroreflection of Retroreflective Sheeting (E 810), ASTM Test Method for Retroreflectance of Horizontal Coatings (D 4061), ASTM Guide to Properties of High Visibility Materials Used to Improve Individual Safety (F 923), and ASTM Specification for Nightime Photometric Performance of Retroreflective Pedestrian Markings for Visibility Enhancement (E 1501).

THE EYE

The Visual System

The human eye functions in a manner similar to a camera. It has a lens to focus images of objects and an iris to control the amount of light that enters (Fig. 3). A complex light-sensitive layer, called the retina, plays a role analogous to that of the film in a camera. Neither the structure of the retina nor its function are fully understood. It contains two different types of light receptors that send information along neural pathways to the visual cortex of the brain. They are called rods and cones because of their shapes. The rods are responsible for black-and-white vision at low light levels; they are not considered further in this section. At usual daylight levels, the rods are overwhelmed and do not contribute to vision. The cones are responsible for color vision. There are three types of cones, each with a different spectral sensitivity. The exact spectral response of each type of cone is not known, although it is assumed that each cone response function is related to the absorption curve of its pigment. The absorption curves are broad and overlapping (Fig. 4). They peak in the short, middle, and long wavelength regions of the visible spectrum; thus the designations blue, green, and red (sensitive) cones are sometimes used.

Detailed models of color vision have been proposed [*10,11*], but they are presently based on incomplete information. What happens to the neural signals from the retina on the way to and in the brain is not well understood, but for most work related to color and appearance, it does not need to be.

Perception

Perception is defined as the translation of retinal images by the observer into meaningful information about the environment. The perception of objects and their colors thus represents the overall response of the visual system, including both the eye and the brain. Vision is called a psychophysical phenomenon—physical in the way light reaches the eye, psychological in how the brain interprets the neural signals. The psychological factor determines, for example, whether a given color combination is interpreted as pleasing or displeasing. The mechanism of seeing is physical; the interpretation of what is seen is psychological.

Objective color measurement is, however, confined to physical aspects. For example, the perceived color of a specimen may be changed by changing the color of the area surrounding it. This phenomenon, called simultaneous contrast, cannot yet be evaluated instrumentally.

Another example of a perceptual phenomenon is chromatic adaptation, defined as the changes in the visual system's sensitivities due to changes in the spectral quality of the illuminating and viewing conditions. These changes tend to compensate, for example, for the effect of the change in illumination from distinctly bluish daylight to distinctly yellowish incandescent lamplight. The colors of familiar objects tend to appear the same (they tend to exhibit color constancy) when the observer goes between environments illuminated by the two kinds of light. Yet the actual colors have all been shifted because of the change in spectral composition of the incident light.

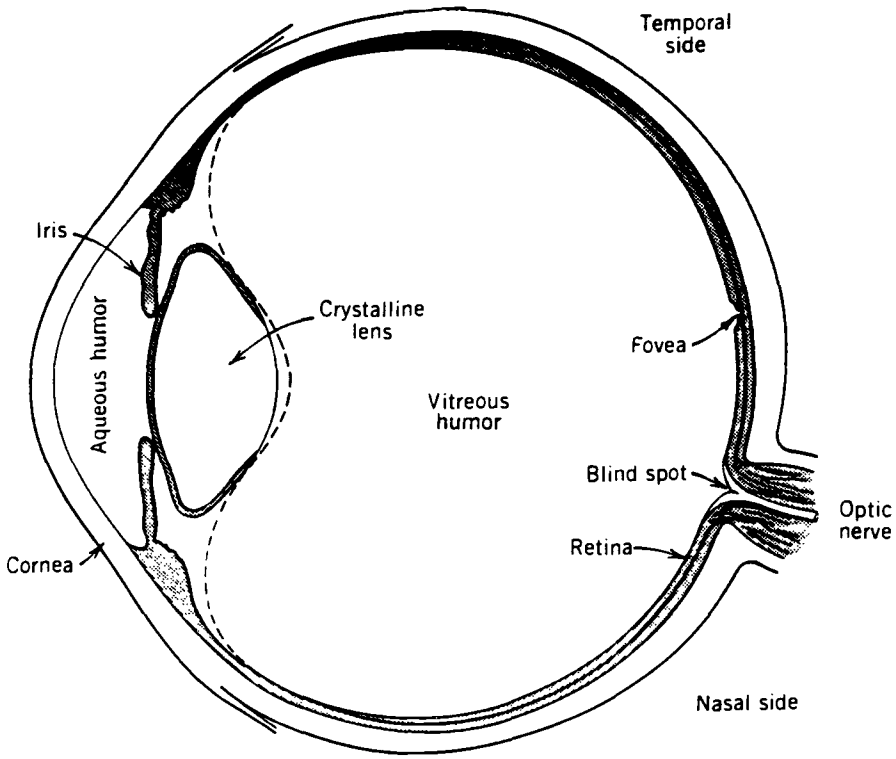

FIG. 3–Cross-sectional diagram of the eye showing features of most interest for color vision [*9*].

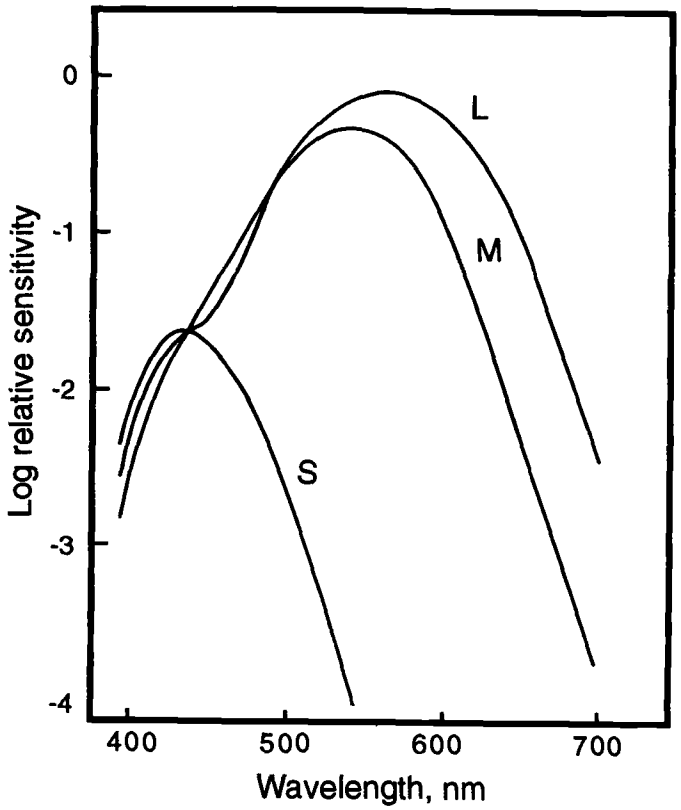

FIG. 4–Spectral curves showing the relative sensitivities of the three types of cones in the eye, peaking in the short (S), medium (M), and long (L) wavelength regions (based on Ref *10*.)

The Variables of Perceived Color

The fact that the eye perceives color because it has three types of cones with differing spectral sensitivities implies, and experience confirms, that perceived color should have three variables. Several sets of these variables are of interest because of their wide use.

Object Colors: Cylindrical Systems

Of great interest to the paint colorist are the variables applying to the perception of object colors. Hue is always one of the variables; the Munsell system (see later in this chapter under **Munsell System**) is an example. Hue is defined as the attribute of color described by common names such as red, yellow, green, blue, etc. The hues are commonly arranged in a circle in the order of their appearance in the spectrum, with the circle closed by the purples, mixtures of the red and blue at the ends of the visible spectrum (Fig. 5).

A second important variable of object colors is lightness, the attribute by which an object is judged to reflect more or less light. It is often represented graphically by a line through the center of the hue circle and perpendicular to its plane (also shown in Fig. 5). The upper and lower ends of this line, often called the neutral or achromatic axis, are white and black, respectively.

The third variable in this set has several different names, referring to variations among what we can perceive: Chroma, saturation, and colorfulness are examples. The common factor among these names is a sense of the amount, in contrast to the kind, of hue in the color. In this section we use chroma as the name for this third variable and show it also in Fig. 5. This quantity is exemplified by the distance between the point representing the color and the neutral axis.

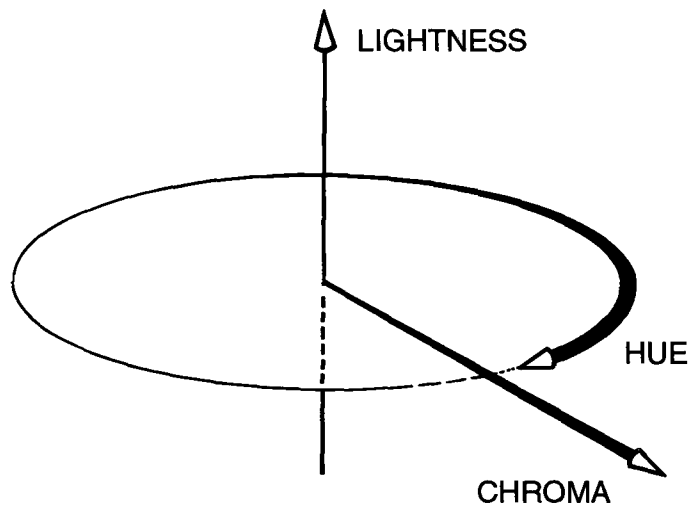

FIG. 5–Arrangement of the hue, lightness, and chroma axes in the usual cylindrical representation of color space.

Colored Lights

When we deal with colored lights instead of objects, two changes need to be made in the above system: Lightness is replaced by brightness and chroma by saturation. Brightness in this sense is defined as the attribute by which an area appears to emit more or less light.

Object Colors: Opponent Systems

A widely used alternative to the hue-lightness-chroma system described above is an opponent-color system that mimics the behavior of the neural signals transmitted from the retina to the brain. The lightness axis, often labeled L, is retained, but the hue circle is replaced by two opponent-type axes at right angles and perpendicular to the lightness axis (Fig. 6). Commonly they are a redness-greenness and a yellowness-blueness axis labeled a and b, respectively, as in the figure. Scales of this type are displayed in many color-measuring systems; examples are given later in this chapter under **COLOR ORDER SYSTEMS**.

Color Constancy and Metamerism

Color Constancy

As previously noted under **Perception**, color constancy is the general tendency of colors to remain constant in appearance when the color of the illumination is changed. Note that this term refers to what happens to the color of a single specimen when the illumination is changed.

Metamerism

Of greater concern to the colorist, because it is of industrial importance and largely under his control, is what happens to the relationship of two colors when the illumination is changed. Suppose, for example, that two colors, matching in

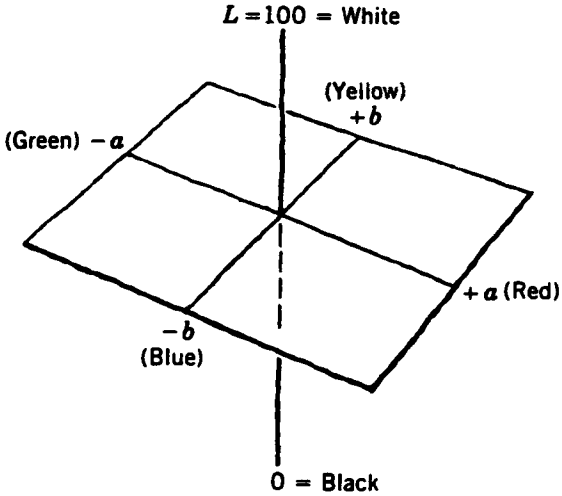

FIG. 6–Arrangement of the lightness, redness-greenness, and yellowness-blueness axes in the usual opponent-color representation of color space [*1*].

daylight, are formulated by using different sets of pigments. The two colors may not match under another type of illumination, such as incandescent lamplight, since the two specimens may exhibit different types and degrees of color constancy. This phenomenon is known as illuminant metamerism, and the colors are said to be metameric. Illuminant metamerism is defined as the property of two specimens having different spectral characteristics (resulting in the example from the use of different pigments; see Fig. 7) and having the same color when viewed under a given source, but different colors when viewed under a different source. Observer metamerism also exists in which two colors match to some observers but not to others.

Only when colors have identical spectral curves can they be expected to match under all types of light and to all observers; this is why the same pigment formulation should be used when remaking the color. Whenever pigments used for the match have different spectral characteristics from those used in the sample, the resultant color match should be tested for the absence of metamerism by several observers and under several different types of illumination, for example, daylight, incandescent lamp light, and fluorescent lamp light, preferably using a color-matching booth. If the match is not satisfactory, spectrophotometric analysis of the two formulations should be carried out to determine their spectral differences, and the new formulation should be adjusted to minimize these differences. ASTM Practice for Visual Evaluation of Metamerism (D 4086) specifies procedures for identifying the presence of metamerism and evaluating it semiquantitatively. Means of minimizing metamerism in both visual and instrumentally aided color matching are described later in this chapter in the section entitled **COLOR MATCHING**.

COLORIMETRY AND THE CIE SYSTEM

Colorimetry is defined as the science of color measurement. Its modern development began in 1931, when, in the interest of standardization and to focus attention on the properties of material objects such as paint films, international standards and recommendations were established by the International Commission on Illumination (Commission Internationale de l'Éclairage, CIE). These recommendations [*12*] define standard lights and observers and a methodology for combining their properties with those of the objects to describe color and related appearance parameters.

CIE Standard Sources and Illuminants

Here it is necessary to note two conventions of CIE terminology [7] reflected in ASTM E 284. A source is defined as a real emitter of light, whereas an illuminant is defined as a

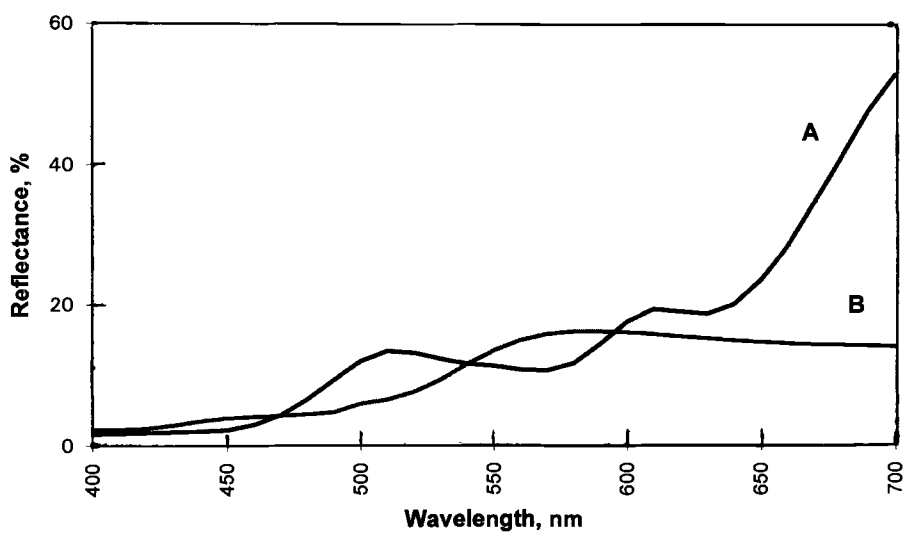

FIG. 7–Spectrophotometric curves of two highly metameric paint films. To most observers, the films match visually and are a dull green color in daylight, but Sample A shifts color to a strong reddish brown in incandescent lamp light while Sample B exhibits color constancy for this change of illumination.

table or figure giving the spectral power distribution of the corresponding source.

Incandescent Source and Illuminant

In 1931, the CIE defined a tungsten-filament incandescent lamp of 2856 K color temperature (see later in this section under **Other Features of the CIE System**) as Source A. Later, when measurement of spectral power distributions became easier, the fundamental definition was changed to the lamp's spectral power distribution, known as Illuminant A. The spectral power distribution of Illuminant A is given in Ref *12*, in a CIE/ISO standard [*13*], and in abbreviated form in ASTM Practice for Computing the Colors of Objects by Using the CIE System (E 308).

Daylight Source and Illuminants

The CIE also recommended in 1931 standard Source C, consisting of liquid filters used in combination with Source A, representing north-sky daylight. Later, the fundamental definition was changed to that of Illuminant C [*12*].

Source and Illuminant C do not duplicate the ultraviolet content of natural daylight and thus do not provide correct daylight color rendition of fluorescent materials. For this reason, the CIE adopted in 1968 a series of standard illuminants duplicating the spectral power distributions of various phases of natural daylight, called the D series. They are designated by their correlated color temperatures (see later in this section under **Other Features of the CIE System**). The most important of these daylight illuminants [*12,13*] is D65, with a correlated color temperature of 6500 K. The spectral power distributions of Illuminant C and several of the D series are tabulated in ASTM E 308. Unfortunately, very few real sources, whether for visual or instrumental use, simulated any of the D illuminants satisfactorily. The CIE has recommended procedures for assessing the quality of daylight simulators [*14*]. The relative spectral power distributions of CIE Standard Illuminants A, C, and D65 are shown in Fig. 8.

Fluorescent Illuminants

In 1986, the CIE defined [*12*], but did not recommend as standard illuminants, a series of twelve spectral power distributions representative of various types of fluorescent lamps, including cool white, lamps simulating daylight well, and three-band lamps. These data should be used when calculations involving fluorescent lamps are required.

CIE Standard Observers

1931 CIE Standard Observer

In order to evaluate colors consistently, a standard observer was defined by the CIE in 1931 [*12,15*] by evaluating the spectral responses of a small group of well-trained individuals. The spectral responses of the CIE 1931 Standard Observer were determined by means of experiments, like those described later in this chapter under **Additive Mixing of Lights**, in which the observer determined the amounts of three primary colors (red, green, and blue) required to match the colors of all wavelengths of the visible spectrum. These sets of three values are called tristimulus values. For convenience, the data were transformed mathematically to correspond to the use of imaginary primary lights designated X, Y, and Z. The Standard Observer is defined by the amounts, $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, and $\bar{z}(\lambda)$, of these primaries required to match the spectrum colors; these are plotted in Fig. 9. The symbol (λ) indicates that the quantity depends on the wavelength, λ. The quantities $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, and $\bar{z}(\lambda)$ are known as the color-matching functions of the 1931 CIE Standard Observer.

The transformation from real primaries to X, Y, and Z was made so that the color-matching function $\bar{y}(\lambda)$ is equal to the spectral luminous efficiency function $V(\lambda)$, that is, the effectiveness of radiation to stimulate the perception of light. This choice means that the tristimulus value Y of a given color, called its luminance, contains all the information about the lightness of the color.

1964 Supplementary Standard Observer

The data for the CIE 1931 Standard Observer were obtained with a visual colorimeter in which the field of view subtended an angle of only 2° at the eye of the observer. This was selected to correspond to the size of the fovea, that part of the retina containing only cones used in color vision. Later, the CIE studied color vision in a 10° field, with the central 2° portion disregarded. This corresponds to sample sizes more like those used in commerce, but for which the spectral sensitivity of the eye is somewhat different from that for the 2° field. With the newer data, the CIE established the 1964 Supplementary Standard Observer [*12,15*]; see also ASTM E 308. Where confusion might result, quantities referring to the 1964 Supplementary Standard Observer are given the subscript 10; for example, its color-matching functions are $\bar{x}_{10}(\lambda)$, $\bar{y}_{10}(\lambda)$, and $\bar{z}_{10}(\lambda)$.

Calculation of Tristimulus Values

The tristimulus values X, Y, and Z of a color can in principle be obtained by direct matching, as were the tristimulus values of the spectrum colors defining the standard observers. But this is impractical, and one of two other methods is always used. One of these involves the design and use of tristimulus (filter) colorimeters and is discussed later in this chapter under **Tristimus (Filter) Colorimeters**. The other requires knowledge of the spectral reflectance curve of the specimen, obtained by spectrophotometry, and the following procedure.

At any wavelength, the contribution to a tristimulus value is given by the product of the relative spectral power of the illuminant, $S(\lambda)$, the reflectance of the specimen, $R(\lambda)$, and one of the color-matching functions of the observer, for example, $\bar{x}(\lambda)$. These products are summed over the visible wavelengths, then normalized by multiplication by a normalization factor k; for example,

$$X = k\,\Sigma\, S(\lambda)\, R(\lambda)\, \bar{x}(\lambda)$$

(and similar equations for Y and Z), where Σ is the sign for summation over the visible wavelength region. The quantity k is chosen to make Y for perfect white equal to 100:

$$k = 100/\Sigma\, S(\lambda)\, \bar{y}(\lambda)$$

The CIE had defined "perfect white" as the perfect reflecting diffuser, the ideal reflecting surface that neither absorbs or transmits light, but reflects all of it. Most textbooks,

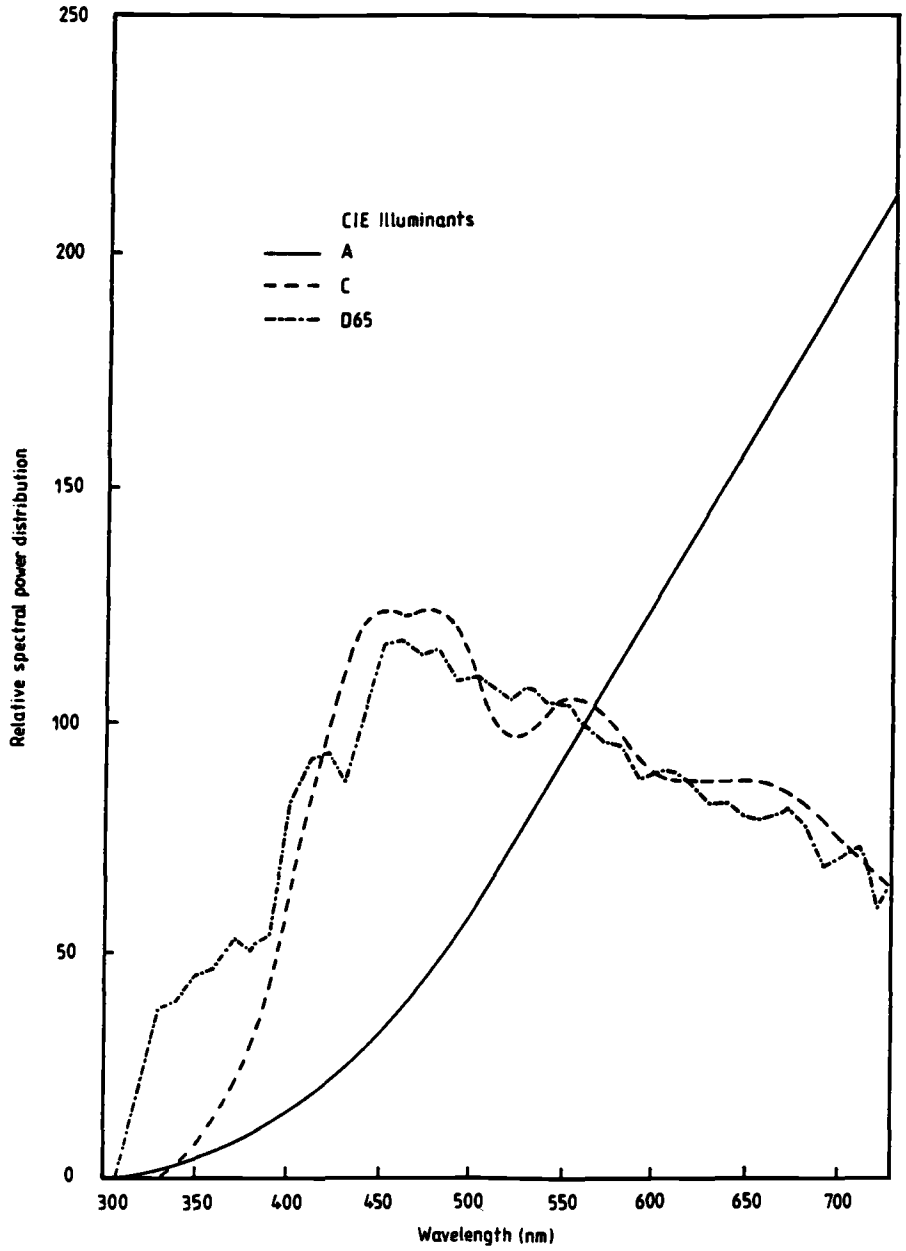

FIG. 8–Relative spectral power distributions of CIE standard Illuminants A (incandescent lamp light), C (north-sky daylight), and D65 (actual daylight) [*6*].

ASTM E 308, and Ref *12* provide examples of the use of these equations. Because the fundamental process is integration, for which summation is an approximation, the process is usually referred to as (tristimulus) integration.

If a large number of sets of reflectance data are to be integrated for the same illuminant and observer, it is convenient to combine quantities such as $S(\lambda)\,\bar{x}(\lambda)$ by multiplying them together and normalizing the products so that $k = 1$. The resulting tristimulus weighting factors can then be stored and used by multiplying them by whatever function $R(\lambda)$ is desired. The CIE has not tabulated or recommended specific sets of tristimulus weighting functions, but a substantial number can be found in ASTM E 308. They may be used for wavelength intervals of 10 or 20 nm. For closer intervals, such as 5 or 1 nm, the tables in E 308, Ref *12*, or Refs *13* and *15* should be used.

Chromaticity Coordinates and Diagram

An important use of the CIE tristimulus values X, Y, and Z is the calculation of coordinates describing the chromaticity of a color, that is, its hue and chroma, ignoring its luminance or lightness. The CIE chromaticity coordinates x, y, and z are computed from the tristimulus values X, Y, and Z by dividing each of these by the sum $X + Y + Z$. Thus $x = X/(X + Y + Z)$, etc. Since $x + y + z = 1$, only two chromaticity coordinates need be given; usually they are x and y. These chromaticity coordinates can be plotted to yield the 1931 CIE x, y chromaticity diagram, shown in Fig. 10, or the 1964 CIE x_{10}, y_{10} diagram for the Supplementary Standard Observer; the two are quite similar.

Features of the chromaticity diagrams include: (1) the locations of the spectrum colors around the horseshoe-shaped

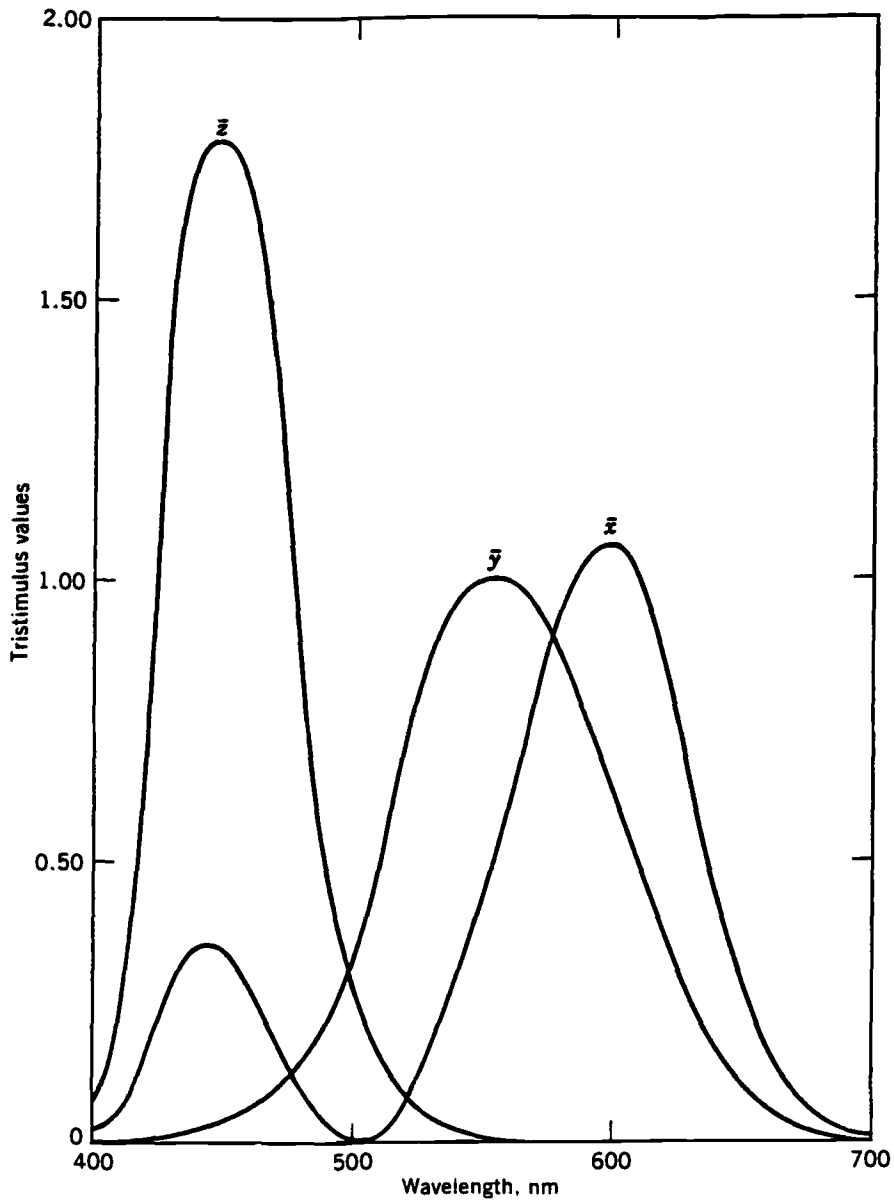

FIG. 9—The color-matching functions of the CIE 1931 standard observer; they are the tristimulus values of the colors of the spectrum [*1*].

spectrum locus, from 400 nm (violet) at the lower left to 700 nm (red) at the right; (2) the straight line along which purples lie joining these two ends of the spectrum locus; and (3) the location of whites (illuminant points) near the middle of the diagram. As an alternative to the three tristimulus values, colors can be specified by the chromaticity coordinates x and y together with the luminance Y (or their equivalents in the 1964 system). These can be arranged in a three-dimensional color space (Fig. 11).

Other Features of the CIE System

Dominant Wavelength, Complementary Wavelength, and Purity

Dominant wavelength is defined as the wavelength along the spectrum locus at the end of a line drawn from the white point (usually Illuminant C) through the sample point to the spectrum locus. For purple colors where the line would end at the purple locus, it is extended back through the white point to the spectrum locus, and the wavelength at that point is designated as the complementary wavelength of the sample. The fractional distance from the white point to the sample point relative to the distance to the spectrum or purple locus is called the (excitation) purity of the sample. Dominant wavelength correlates well with the hue of the sample, but purity does not correlate well with any perceived quantity and is little used today.

Blackbody Locus, Color Temperature, and Correlated Color Temperature

When a metal, such as a lamp filament, is heated, it first radiates heat in the infrared region, then light with a chromaticity at the red corner of the diagram. As it gets hotter, the chromaticity shifts through the oranges and yellows. The line

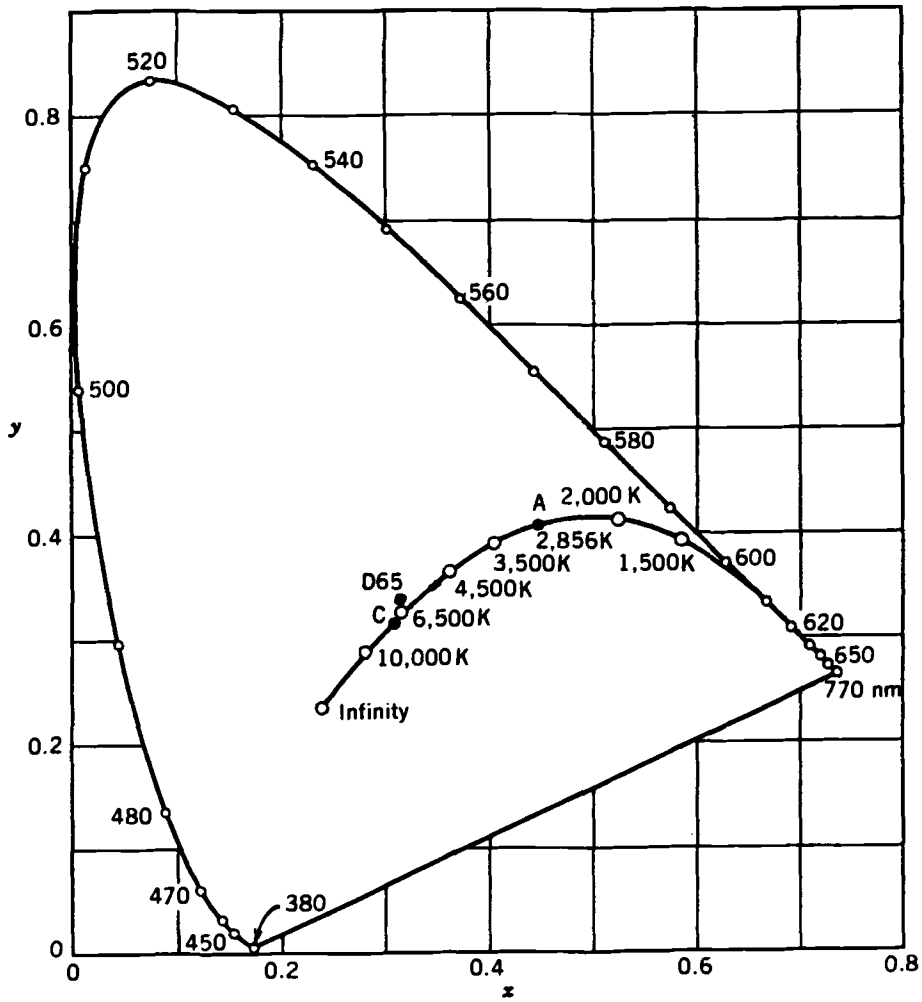

FIG. 10—The CIE 1931 *x,y* chromaticity diagram showing the various features described in the text [*1*].

along which these chromaticities lie for perfect absorbers and emitters of radiation is called the blackbody locus and is shown in Fig. 10. If the metal did not melt, its color would continue along this locus through white to light blue at infinitely high temperature. The temperature of a perfect blackbody can be correlated with its chromaticity and is called the color temperature of the body. It is measured in kelvins, K; the color temperature of Illuminant A is, for example, 2856 K. Many light sources, including the phases of daylight and fluorescent lamps, have chromaticities that are close to, but not on, the blackbody locus. In that case, the color temperature closest to the chromaticity of the source is used and called its correlated color temperature. An example is Standard Illuminant D65, with a correlated color temperature of 6500 K.

Uniform Color Spaces

From almost the beginning of the CIE system, it was recognized that distances in the CIE space did not correlate well with visual estimates of the magnitudes of color differences. Many proposals have been made for deriving quantities that are more uniformly visually spaced. In 1976, the CIE recommended two more nearly uniform color spaces that, although not perfect, have been widely used. Here we describe the one that is most widely used in the paint and related industries and mention briefly the second, more useful when colored lights are considered. The equations for these two spaces, known by official acronyms CIELAB and CIELUV, are found in Refs *1* to *6* and *12* and in ASTM E 308.

CIE 1976 L*, a*, b* *(CIELAB) Space*

CIELAB is an opponent-type color space, with a lightness axis L^*, a redness (positive values)-greenness (negative) axis a^*, and a yellowness (positive)-blueness (negative) axis b^*, all mutually perpendicular, as illustrated in Fig. 6. The transformations from Y to L^*, from X and Y to a^*, and from Z and Y to b^* are all nonlinear, using cube-root functions.

The equations for these transformations are:

$$L^* = 116\,(Y/Y_n)^{1/3} - 16$$

$$a^* = 500\,[(X/X_n)^{1/3} - (Y/Y_n)^{1/3}]$$

$$b^* = 200\,[(Y/Y_n)^{1/3} - (Z/Z_n)^{1/3}]$$

where X_n, Y_n, and Z_n are the tristimulus values of the illuminant or white point, and there are some restrictions on the

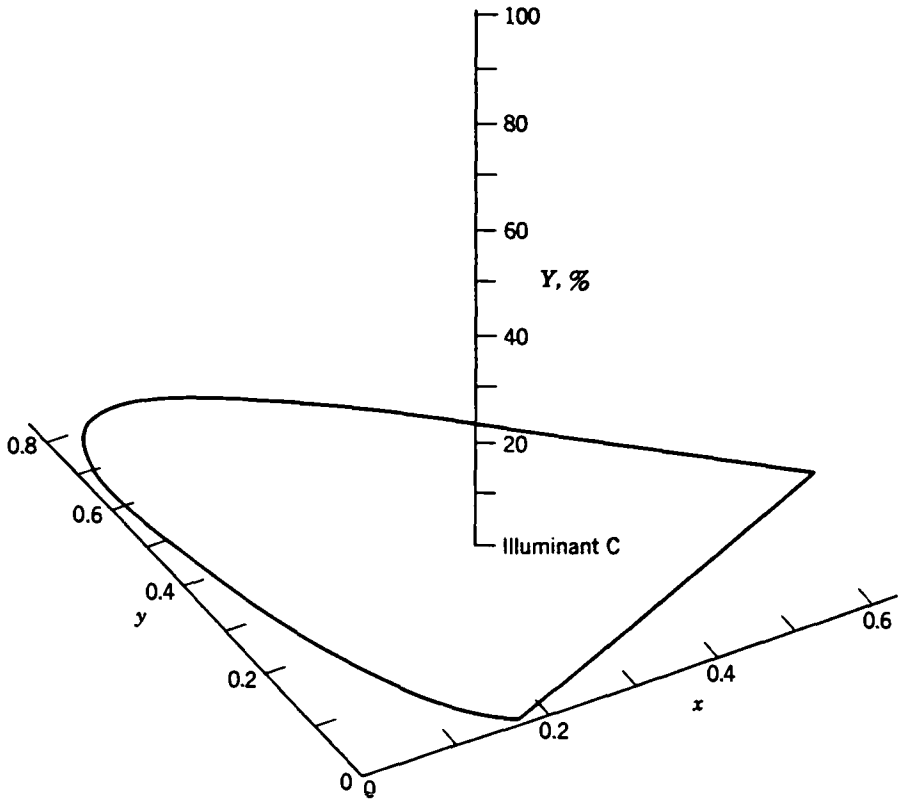

FIG. 11—A three-dimensional representation of CIE color space with the luminance (lightness) axis *Y* rising above the chromaticity diagram [*1*].

use of the equations for very small values of X, Y, or Z described in the references cited above.

Because CIELAB does not have tristimulus values or chromaticity coordinates as defined for the 1931 and 1964 CIE systems in **Chromaticity Coordinates and Diagram**, it does not have a chromaticity diagram.

An alternative set of CIELAB coordinates retains L^* but combines a^* and b^* to give chroma C^* and hue angle h (measured in degrees):

$$C^* = (a^{*2} + b^{*2})^{1/2}; \quad h = \tan^{-1}(b^*/a^*)$$

These correlate well with visual judgments of lightness, chroma, and hue, respectively. Perhaps the widest use of CIELAB is in the calculation of color differences (see later in this chapter under **Color Difference Calculations**).

CIE 1976 L*, u*, v* *(CIELUV) Space*

The CIELUV space has a chromaticity diagram with coordinates u' and v', which are linear transformations of x and y, respectively. The linearity is important for the additive mixing of colored lights (see later in this chapter under **Additive Mixing of Lights**). For the three-dimensional CIELUV space, these are combined with the (nonlinear) L^* transformation to give opponent-type axes u^* and v^*, whose meanings are the same as those of CIELAB a^* and b^*, respectively. An alternative set of hue angle and chroma coordinates, like those in CIELAB, and a color-difference equation, much less widely used than the CIELAB equation, are also part of this system.

COLOR ORDER SYSTEMS

In this section are discussed briefly the major color order systems, consisting of physical exemplifications or atlases illustrating underlying systems. References *16* and *17* provide useful general coverage.

Munsell System

Dating from the early 1900s, the Munsell system is accepted by most users as the standard for equal visual spacing. It is described in ASTM Test Method for Specifying Color by the Munsell System (D 1535). Its color solid is like that of Fig. 5 with the sole exception that lightness is called *value* in the Munsell system. Munsell Hue is designated by position around the hue circle in a notation combining letters designating five major hues (red, yellow, green, blue, purple) and their pairs (R, YR, Y, GY, G, BG, B, PB, P, RP) with numbers from 1 to 10. Munsell Value, to which CIE lightness L^* is a good approximation, runs from zero for black to 10 for white. Munsell Chroma, which expresses the degree of departure of the color from the gray of the same lightness, starts at zero and is open-ended. To describe a color in the Munsell system, the hue, value, and chroma are noted in a prescribed sequence, as for example, 8R 4/10. This designation indicates that the hue is red (toward yellow-red), the value is 4, and the chroma is 10.

The *Munsell Book of Color* is available in two collections of painted color chips. The glossy finish collection contains approximately 1600 removable chips, the matte collection ap-

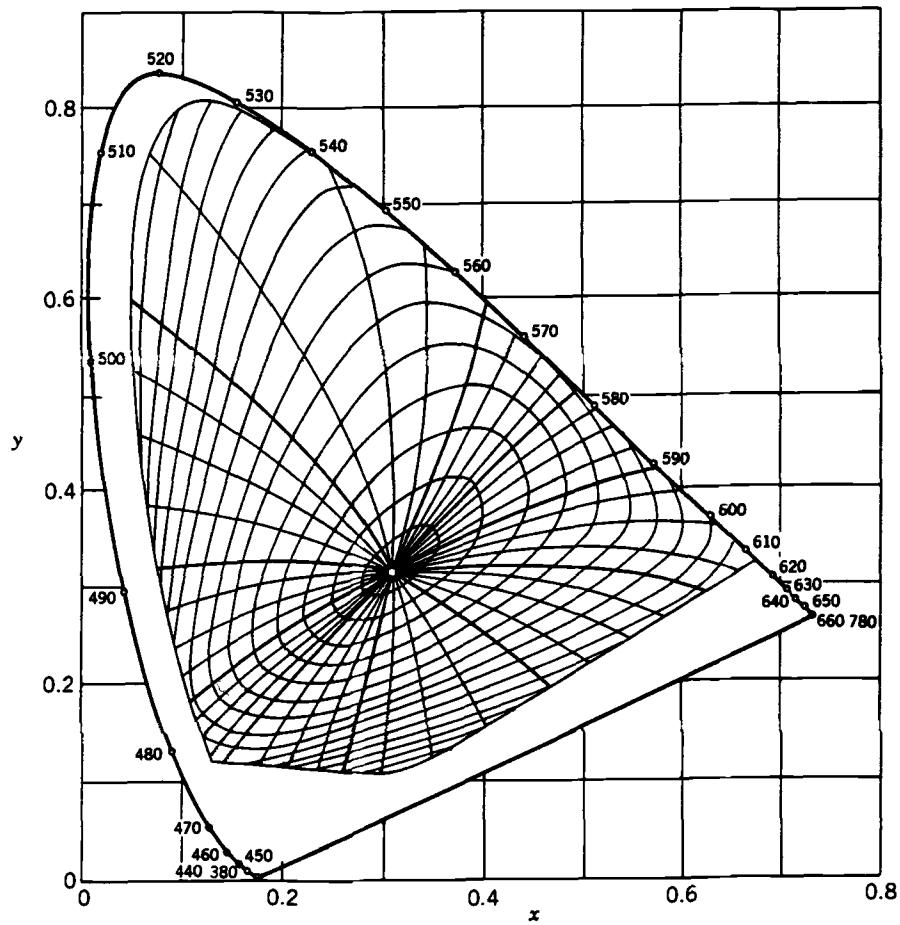

FIG. 12–Lines of constant Munsell Hue and closed curves of constant Munsell Chroma, at Munsell Value 5 plotted on the CIE 1931 chromaticity diagram [*19*].

proximately 1200 permanently mounted chips. The chips are arranged on pages of constant Munsell Hue; in any one row they are perceived as having the same Munsell Value and in any one column as having the same Munsell Chroma when viewed under daylight illumination on a medium-gray background. The colors progress from very light at the top to very dark at the bottom and from neutral at the left to high chroma at the right (or the reverse on facing pages). In 1943, the underlying Munsell system was defined in colorimetric terms [*18*], and since 1968 the chips in the glossy editions of the *Munsell Book of Color* have been produced to match these specifications. Figure 12 shows contours of equal Munsell Hue and Chroma at Value 5 on the 1931 CIE x, y chromaticity diagram.

ISCC-NBS System

In the 1950s the Inter-Society Color Council (ISCC) and the National Bureau of Standards (NBS) developed the ISCC-NBS Method of Designating Colors [*20*] based on the Munsell system but grouping similar colors to produce a smaller number (267) of categories. These are designated by descriptive color names, for example, dark reddish orange for the group containing 8R 4/10.

Universal Color Language

The Munsell system and the ISCC-NBS system are both parts of a Universal Color Language [*20*], a six-level system for describing color to any desired degree of accuracy. Level 1 consists of the use of 13 hue and neutral names. At this level, the color with Munsell notation 8R 4/10 would be described as orange. In Level 2, which has 29 categories, intermediate hue names are added. Here the color would be described as reddish orange. Level 3 is the ISCC-NBS system, and Level 4 is the Munsell system as used in the *Munsell Book of Color*; designations at these levels are given above. Level 5 uses interpolated Munsell notations based on visual comparison of the color with *Munsell Book* chips. With practice it is possible to interpolate accurately to 1/10 value step, 1/4 chroma step, and from 1 hue step at chroma /2 to 1/4 hue step at chroma near /10 and above. Thus, at this level the color might be designated very accurately as 8.25 R 4.1/9.75. The final stage, Level 6, of the Universal Color Language is based on the results of color measurement, expressed as CIE chromaticity coordinates x, y, and Luminance Y. Now the color might be specified with greatest accuracy as $x = 0.527$, $y = 0.343$, $Y = 12.5$.

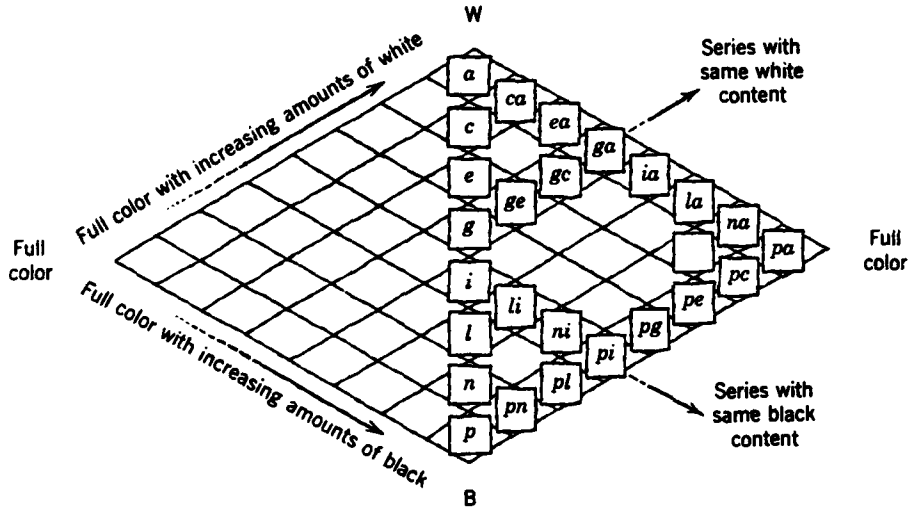

FIG. 13–Two opposing constant-hue pages in the Ostwald system [*1*].

Ostwald System

This system [*21*], which is not illustrated by any set of samples now commercially available, consists of 24 charts of approximately constant hue containing sets of chips having nearly constant chroma but different lightnesses. The chips are arranged (Fig. 13) on each chart in a triangular array, as shown. The most important atlas based on the Ostwald system in the United States was the *Color Harmony Manual*, available in the 1940s and 1950s [*22*].

DIN System

The DIN Color System is the official German Standard Color System [*23*]. Its coordinates are hue (for which dominant wavelength is used), saturation (like chroma except representing difference from black instead of from gray of the same lightness), and relative darkness. Contours of constant DIN hue and saturation, applicable to all lightness levels, are shown on the 1931 CIE x, y diagram in Fig. 14. From time to time, atlases of DIN samples have been available in glossy and matte finish and in transparent films. In the former two, chips are arranged on pages of constant hue, similar to the Munsell arrangement.

Natural Color System

Developed in the late 1960s and 1970s, the Natural Color System (NCS) [*24*] is the national standard color order system in Sweden and several other European countries. It is based on an entirely different principle from that of the other systems discussed, namely the resemblances of colors to six imaginary elementary colors, unique red, yellow, green, and blue, and black and white. The four hues are placed 90° apart on the hue circle. This does not lead to visually equal hue spacing. Two opponent-type axes result, perpendicular to the black-white lightness axis. The third variable of the system is chromaticness.

In terms of resemblances, hue is defined as the resemblance of a color to the two nearest chromatic elementary colors. For example, an orange might be said to have 80% resemblance to red and 20% to yellow; its hue notation would be Y80R. Chromaticness is the resemblance of the color to the (imaginary) color of the same hue having the maximum possible chromatic content. Lightness is not an explicit variable in the system; the third resemblance can be to either white or black. Scales of resemblances to white, black, and the aforementioned maximally chromatic color are chosen so that these three add to 100%, so only one of the resemblances to white or black need be specified. For the notation, resemblance to black has been selected, so that the three variables of the system are blackness, chromaticness, and hue. The complete NCS notation for the orange sample considered above in the Munsell system, for example, is approximately 3070 YBOR.

In the NCS atlas, pages of constant hue notation contain chips arranged on a grid in the form of an equilateral triangle, as shown in Fig. 15. Note that there is a similarity to the Ostwald triangle, the difference being that in the Ostwald system the corner points are real samples; in the NCS, they are imaginary elementary colors. The NCS is subsidized by the Swedish government and aggressively marketed, and thus is available at lower cost than most other atlases.

OSA-UCS System

The Optical Society of American Uniform Color Scales system [*25,26*] was developed by a committee of the OSA between 1947 and 1976. Although the committee concluded that no perfectly equally visually spaced system can exist because color space itself is not Euclidean, it attempted to achieve the best possible compromise and is generally thought to have succeeded. The 558 samples of the OSA atlas are arranged in a rhombohedral lattice in which each sample, except those at the edges, has twelve nearest neighbors. The axes of the color solid are lightness, L (with both positive and negative values around zero at middle gray) and two opponent axes, j (from the French *jaune* for yellow), with positive values toward yellow and negative values toward purple-blue, and g (for greenness), with blue-greens at the positive end and

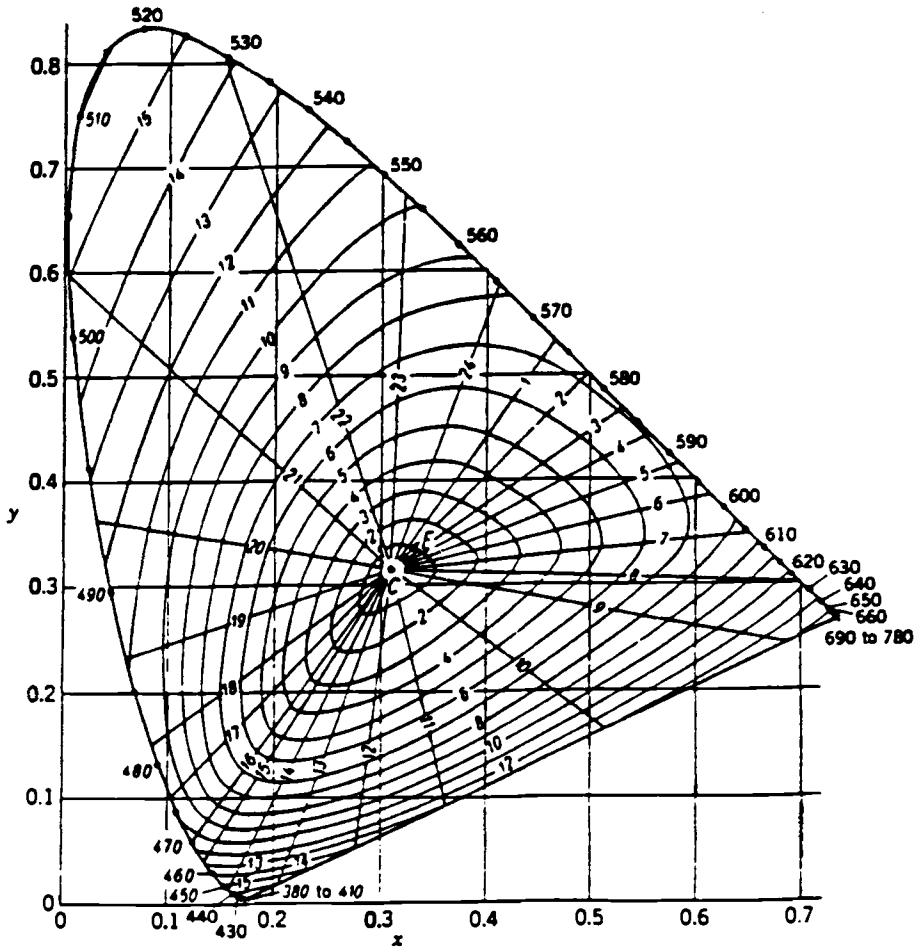

FIG. 14–Lines of constant DIN hue and closed curves of constant DIN saturation on the CIE 1931 chromaticity diagram. The figure applies to all DIN darkness levels [*16*, modified from *23*].

pinks at the negative end. One of the features of the lattice is the existence of many planes of closely related samples, sometimes varying along all three axes, that appear strikingly beautiful.

The OSA-UCS system is described in ASTM Practice for Specifying Color by Using the Optical Society of America Uniform Color Scales System (E 1360). A portion of the OSA-UCS lattice illustrating the arrangement of samples is shown in Fig. 16, and Fig. 17 shows the spacing of samples of the $L = 0$ plane on the 1964 CIE x_{10}, y_{10} diagram.

Colorcurve System

This new color order system was introduced in the United States in 1989. It is based on a color space similar to CIE 1964 tristimulus space [*27*]. Aim points are laid out according to additive mixing (see subsection later in this chapter entitled **Additive Mixing of Lights**) of CIE 1964 tristimulus values X_{10}, Y_{10}, Z_{10} for Illuminant D65, starting from eight specified CIELAB points. The CIELAB lightness axis L^* (designated only as L) is retained, but coordinates along the CIELAB-type opponent axes are replaced by a simple numbering system giving the sample location in terms of the number of lattice steps between it and the neutral axis in the directions of two adjacent major axes directed toward reds, yellows, greens, and blues. A typical Colorcurve notation would be L40 R1Y3, representing at lightness level 40 the lattice point one step away from neutral toward the reds and three steps toward the yellows. This is an orange only slightly different from the sample discussed above. The Colorcurve atlas contains about 2200 painted samples.

Another feature of the Colorcurve system is that spectral reflectances are furnished for the aim points. These can be additively mixed like tristimulus values to obtain the spectral curve corresponding to any Colorcurve notation; this can be the basis for computer colorant formulation (see subsection later in this chapter entitled **Instrumental and Computer-Aided Color Matching**) to provide a match with minimum metamerism to the surrounding Colorcurve samples. ASTM Practice for Specifying and Matching Color Using the Colorcurve System (E 1541) describes the system in more detail, including a tabulation of spectral reflectances, tristimulus values, and CIELAB coordinates for the sample aim points.

Printed Systems

For each of the color order systems described above, atlas samples consist of painted chips individually matched to the

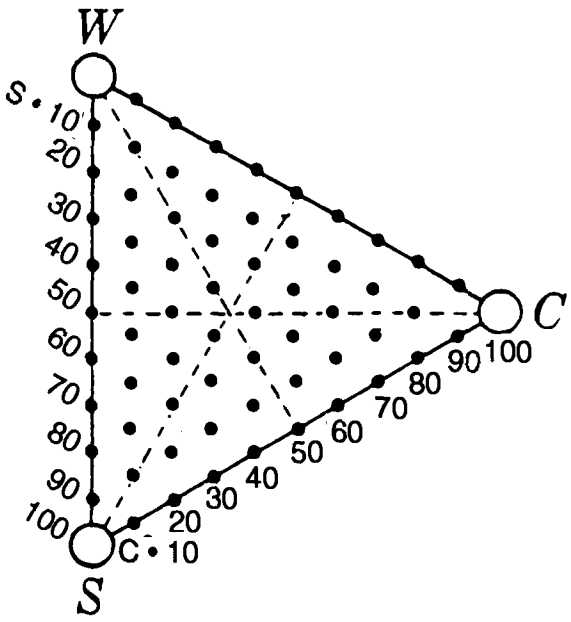

FIG. 15–Arrangement of colors on a constant-hue page in the NCS system. They are located according to their resemblances to ideal white (W), ideal black (B), and the imaginary Color C having 100% chromaticness [*24*].

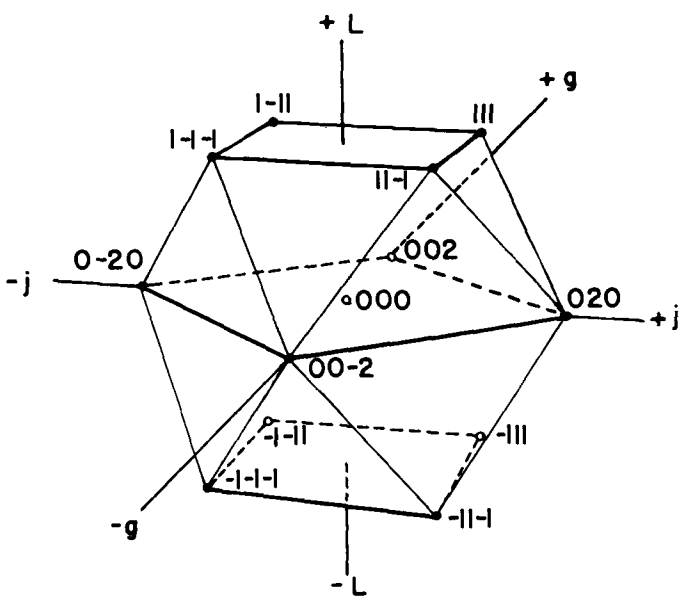

FIG. 16–Cuboctahedron around the center point of the OSA system showing its three axes, ± *L* (lightness), ± *j* (yellowness-blueness), and ± *g* (greenness-redness). There are twelve nearest neighbors around the center point, with the *L,j,g* coordinates shown. The entire OSA space is formed by extending this figure in all directions [*16*].

specified aim points with a mean accuracy of about one CIELAB unit. Many other collections, produced by printing, exist. Of necessity, they all have the characteristic that large groups of samples are produced at the same time; it is not possible to adjust the color of each one individually for closest conformance to the aim point. In many instances average accuracy is much poorer than that for the painted atlases,

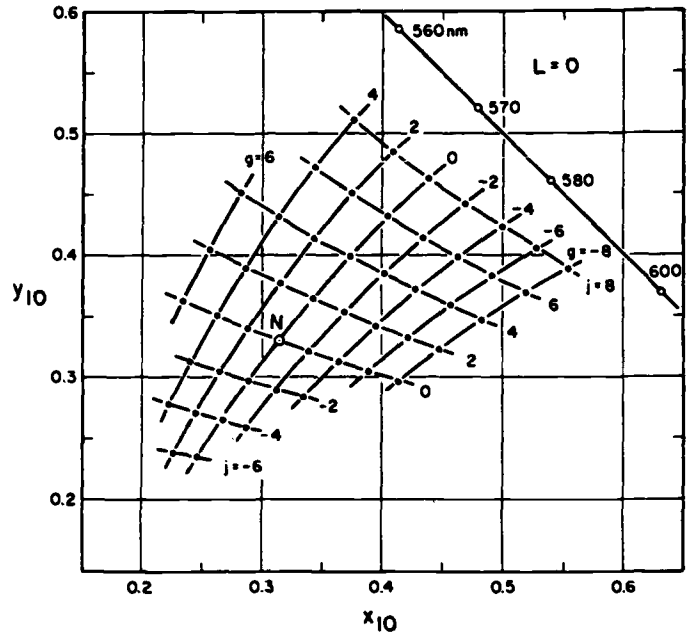

FIG. 17–Section of the CIE 1964 x_{10}, y_{10} diagram showing the locations of points on the *L* = 0 plane of the OSA system (ASTM E 1360, from Ref *3*).

and it is especially difficult to reproduce the samples accurately in subsequent printings or editions. Their cost is, however, relatively low.

Single-Number Color Scales

Occasions arise in which the colors of samples vary along a single direction in color space. In such a case the color can be described adequately by a single scale value. Three cases are of interest: whiteness, yellowness, and series ranging from colorless to highly colored as the concentration of a colored component increases.

Whiteness Indices

Whiteness scales start at the point corresponding to an ideal white, which may be the perfect reflecting diffuser (see subsection earlier in this chapter entitled **Calculation of Tristimulus Values**) or some other industry standard, often assigned a whiteness of 100. From this number are subtracted amounts corresponding to departures toward lower lightness and the addition of chromaticness. For example, in ASTM Test Method for Indexes of Whiteness and Yellowness of Near-White, Opaque Materials (E 313), the recommended equation for whiteness index *WI* can be expressed in terms of CIE 1931 tristimulus values for Illuminant C as

$$WI = Y - 4(0.847Z - Y)$$

The first term is the luminance, *Y*, which approximates perceived lightness, and the second term is a measure of departure from white toward yellow. The CIE has defined a whiteness index [*12*] as

$$W = Y + 800(x_n - x) + 1700(y_n - y)$$

where x and y are the 1931 chromaticity coordinates of the sample with lightness Y, and x_n and y_n are the values for the

illuminant point. CIE 1964 values can also be used. This equation allows for departures from white in any hue direction, weighted by the factors shown. In each case the value for the perfect white is 100.

Yellowness Indices

Indices of departure from achromatic toward yellow are formulated similarly to the second term in the ASTM E 313 WI equation given above. The indices start at zero and increase as yellowness increases. In ASTM E 313, the yellowness index YI is given by

$$YI = 100(1 - 0.847Z/Y)$$

A similar equation, given in ASTM Test Method for Yellowness Index of Plastics (D 1925), includes the effect of change in tristimulus value X as well as Y and Z

$$YI = 100[(1.28X - 1.06Z)/Y]$$

This equation is equally applicable to paint films.

Scales for Liquids

When only a limited range of color is involved, for example, in the testing of the color of oil, clear varnish, lacquer, or solvents used in the paint industry, simple methods are used consisting of comparison of the specimen with standard colored solutions or glasses ranging from colorless to highly colored. A standardized series of these colors is used to provide a specialized color scale. The color is often a measure of concentration of ingredient. One difficulty in the use of these special color scales is that the color of the specimen may not match that of the standard; this can make rating on a single-number scale difficult. Nevertheless, their simplicity, low cost, and adaptability to special situations has resulted in wide use of single-number scales for certain applications. Among such scales useful to the paint industry are those described in ASTM Test Method for Saybolt Color of Petroleum Products (Saybolt Chromometer Method) (D 156), ASTM Test Methods for Soluble Nitrocellulose Base Solutions (D 365), ASTM Test Method for Color of Clear Liquids (Platinum-Cobalt Scale) (D 1209), ASTM Test Method for ASTM Color of Petroleum Products (ASTM Color Scale) (D 1500), ASTM Test Method for Color of Transparent Liquids (Gardner Color Scale) (D 1544), ASTM Test Method for Color of Solid Aromatic Hydrocarbons and Related Materials in the Molten State (Platinum Cobalt Scale) (D 1686), and ASTM Test Method for Measurement of Color of Low-Colored Clear Liquids Using the Hunterlab Color Difference Meter (E 450). These and other single-number color scales were intercompared [*28*].

INDUSTRIAL COLOR MEASUREMENT

Instruments Using the Eye as Detector

The eye is the ultimate arbiter in color evaluation because, of course, it passes the final judgment on the acceptability of a color. The first color-measuring instruments used the eye as detector, and this practice is still followed when use of a simple color comparator suffices, as in many of the test methods for single-number color scales described in the preceding paragraph. But there are many factors, such as fatigue, poor color memory, and subjectivity, as well as the perceptual phenomena described earlier under **Perception**, that make the eye at least suspect for close color evaluation work. Therefore the use of the eye as detector has been almost entirely replaced by the use of two types of photoelectric instruments developed since the 1940s for color measurement.

Spectrophotometers

Spectrophotometers provide detailed information on the color properties of specimens, in the form of spectral reflectances (or transmittances), required for the calculation of CIE tristimulus values and derived color coordinates, as described earlier under **Colorimetry and the CIE System** and in ASTM E 308. Spectrophotometers are described here and their abridgments in the form of tristimulus (filter) colorimeters in the next section.

When radiation strikes a sample, it may be reflected, absorbed, or transmitted. Each of these can be measured by most spectrophotometers. All spectrophotometers consist of a light source, a monochromator, arrangements for illuminating and viewing the sample, a photodetector, and an output device. In modern instruments, the latter consists of a computer that processes the signals from the detector and provides for the calculation of tristimulus values and a wide variety of other color-related quantities. Each of these components is described briefly.

Light Source

In most cases the exact nature of the light source in a spectrophotometer is of little importance as long as it has adequate power and stability at all wavelengths in the visible spectrum. Incandescent lamps or xenon flash tubes are widely used. When fluorescent samples are measured (see earlier under **Fluorescence**), the source must illuminate the sample directly and may be filtered to simulate a standard source, such as CIE daylight D65. Most color measuring spectrophotometers are designed with these features. ASTM E 991 provides more information on the measurement of fluorescent samples.

Geometry of Illumination and View

In most spectrophotometers, the geometry of sample illumination and viewing follows CIE recommendations [*12*]. Two standard geometries are widely used. In hemispherical geometry, light from the source usually illuminates the white interior of a hollow, approximately spherical cavity called an integrating sphere, and the diffused light from the sphere illuminates the sample from all angles in the hemisphere bounded by its surface. The sample is viewed at an angle near the normal or perpendicular to its surface. If the sample is glossy, the specular or mirror reflection from its surface will result in a portion of the wall of the integrating sphere also being viewed. The user is given the option of making this part of the sphere white, thus including the specular component, or black, excluding it.

In bidirectional geometry, illuminating and viewing are at angles along the normal to the sample surface (designated 0°) and 45° from the normal, or the reverse. The use of

bidirectional geometry with the specimen illuminated by white light is required when fluorescent samples are measured. Hemispherical and bidirectional geometries are described in ASTM Guide for Selection of Geometric Conditions for Measurement of Reflection and Transmission Properties of Materials (E 179) and in ASTM E 1164 as well as by the CIE [*12*].

In typical 45/0 or 0/45 geometry, several illuminating or viewing beams, distributed around the azimuth at 45° to the normal, may be used. When a specimen exhibits directionality, that is, its reflectance changes when it is rotated in its own plane, the use of an instrument with multiple beams provides data that average over the directionality, giving a single number characteristic of the average properties of the specimen. If it is desired to measure the directionality, an instrument with one illuminating (or viewing) beam, or two 180° apart in azimuth, should be used and measurements made at several different specimen orientations.

For the measurement of specimens exhibiting goniochromatism, in which the reflectance changes when the illuminating or viewing angles are changed, the use of special instruments capable of measuring at different combinations of these angles is required. Several such multiangle instruments, known as goniospectrophotometers, are commercially available. To date, no firm recommendations have been made on the number of combinations or the optimum angles required to characterize such goniochromatic specimens. Such specimens of interest in the paint industry include the so-called metallic and pearlescent coatings for the automotive industry.

Monochromator, Detector, and Output

The light reflected or transmitted by the specimen is directed to the monochromator, in which a narrow (typically 10 to 20 nm) band of wavelengths is selected from the full spectrum of the incident light. The monochromators in modern instruments usually use holographic diffraction gratings or interference filters to isolate the narrow wavelength range. Spectral light is received by the detector, usually a silicon photodiode. Detection may be accomplished by an array of diodes, each positioned permanently to receive light of a given wavelength, thus eliminating the need for a spectrum scanning device. The electrical signal from the detector is usually amplified, digitized, and entered in an interfaced computer. In addition to ASTM E 1164, the following test methods cover the operation of modern spectrophotometers: ASTM E 1331, E 1348, and E 1349.

Spectroradiometers

Instruments closely related to spectrophotometers but made to measure light incident from external sources are known as spectroradiometers. They could be used in the paint industry when, for example, the specimen must be sensed remotely after illumination external to the instrument. Methods for making such measurements are described in ASTM Practice for Obtaining Spectroradiometric Data from Radiant Sources for Colorimetry (E 1341) and ASTM Practice for Obtaining Colorimetric Data from a Visual Display Unit Using Colorimeters (E 1455).

Obtaining Tristimulus Values from Spectral Data

The first step in utilizing spectral data is the calculation of CIE tristimulus values, as described earlier under **Calculation of Tristimulus Values**. This step is performed automatically as part of the measurement sequence in all modern spectrophotometers designed for color measurement. It is usual that the spectral bandpass of the monochromator and the measurement interval are selected to be the same. For highest accuracy, the correct set of tristimulus weighting factors, corresponding to the instrument bandpass, selected from among those added to ASTM E 308 in 1994, must be used in calculating tristimulus values. In addition, the user must select the standard illuminant and the standard observer used, and (when hemispherical measuring geometry is utilized) select the inclusion or exclusion of the specular component in reflectance measurement.

Spectrocolorimeters

Some spectrophotometers are designed so that the measured spectral reflectances or transmittances cannot be accessed for examination; only the resulting tristimulus values and other color coordinates can be printed out. Such instruments are designated spectrocolorimeters.

Tristimulus (Filter) Colorimeters

Among the earliest photoelectric color-measuring instruments were those in which the source-filter-photodetector combinations duplicate the tristimulus functions of the Standard Observer and a CIE Standard Illuminant, usually Illuminant C [*29*]. How well their filters are designed and matched to the spectral characteristics of the source and of the detector determines how accurately the instrument performs. Today a high degree of accuracy is attained in the resulting tristimulus values.

Because of their ease of operation, good precision, and relatively low cost, tristimulus (filter) colorimeters have found wide application for industrial control. They are used primarily as color-difference meters to evaluate the difference in color between a production specimen and a standard of similar spectral character. This last limitation is important for most colorimeters. Because of their design, most colorimeters provide colorimetric data for only one combination of illuminant and observer and therefore cannot detect metamerism. When specimens are metameric, a colorimeter can give incorrect data on the differences among them. Filter colorimeters should not be used to evaluate pairs of specimens that may be metameric. This limitation should be clearly understood.

The use of colorimeters is described in ASTM E 1347. This standard replaces ASTM Test Method for Directional Reflectance Factor, 45-deg 0-deg, of Opaque Specimens by Broad-Band Filter Reflectometry (E 97) (discontinued in 1992).

Selection and Calibration of Instruments

The potential user of color-measuring instrumentation must consider with care the selection of the proper instrument(s), depending on his samples and measurement needs. ASTM E 179 and ASTM Practice for Identification of Instrumental Methods of Color or Color-Difference Measurement

of Materials (E 805) address this topic. They should be consulted, if possible, before the purchase of a new instrument.

The user of any color-measuring instrument must give regular attention to its calibration. Appropriate calibration standards, available from instrument manufacturers and, in some cases, national standardizing laboratories, should be obtained, maintained in good condition, and used at frequent intervals in an established routine [*30*]. A collaborative reference program [*31*] is available by means of which a user's instrument performance can be compared to that obtained for the same samples by the color community as a whole and by national standardizing laboratories.

With proper calibration and maintenance, modern color-measuring instruments are capable of a repeatability and reproducibility far greater than the repeatability with which the samples themselves can normally be prepared for industrial measurement. Thus, special care must be taken to establish a highly reproducible method of paint sample preparation and to establish by careful measurement and periodic verification the uncertainties associated with this step in the measurement process. ASTM standards that deal with these matters are E 1164, E 1331, ASTM Practice for Reducing the Effect of Variability of Color Measurement by Use of Multiple Measurements (E 1345), E 1348, and E 1349. See also ASTM Practice for Selection of Coating Specimens and Their Preparation for Appearance Measurements (D 3964) and Standard Guide for the Preparation, Maintenance, and Distribution of Physical Product Standards for Color and Geometric Appearance of Coatings (D 5531).

The following two subsections apply mainly to spectrophotometers.

Precision

The modern age of computer-interfaced color measuring spectrophotometers began in the mid-1970s. By then it had been clearly demonstrated that such instruments could surpass the eye in the precision of color measurement. Repeatability of instrumental color measurement is about 0.1 CIELAB unit of color difference [*32*] (see later in this chapter under **Color Difference Calculations**). The average reproducibility within a group of similar instruments is about 0.2 CIELAB units [*33*]. Note that 0.5 CIELAB unit is approximately the smallest difference that can be detected visually. Repeatability and reproducibility values are published in the Precision and Bias section of ASTM E 1164.

Bias

This quantity, the difference between a measured result for a standard sample and the result when it is measured in a reference laboratory, is difficult to quantify in the color field where there are no "absolute" values. It is usual to accept the results obtained in a national standardizing laboratory as the reference. On this basis, when instruments are selected to minimize differences in measuring geometry and are properly calibrated and used, the average bias for a group of standard samples can be as low as 0.5 CIELAB unit [*34*]. In addition, the differences between the two sets of measurements can be utilized effectively to model and correct the systematic spectrophotometric errors leading to the bias [*35*].

Commercial Instruments

Instrument design changes have been so frequent in recent years that published information in a manual such as this would almost certainly become obsolete by the time the manuscript is printed. For this reason, detailed information on suppliers and their instrumentation is not included. Such information, including types of instruments manufactured and their design features and performance characteristics, can best be found by first consulting buyers' guides [*36,37*] that are revised annually. Another useful source of information is the lists of exhibitors at paint shows, such as the descriptions published annually in the *Journal of Coatings Technology*. In contacting suppliers of instrumentation, the user might request that they send literature, measure samples sent them, or have a representative visit the user to demonstrate the instrument. Another procedure is to negotiate a rental-purchase contract. While some suppliers are reluctant to negotiate such contracts, the procedure provides users the opportunity to evaluate the instrument with their own operators at their own facilities. Most major manufacturers currently in the field supply both spectrophotometers and colorimeters meeting the descriptions given earlier under **Spectrophotometers** and **Tristimulus (Filter) Colorimeters**.

Several recent trends provide insight into possible future developments in color-measuring equipment and its uses. These trends can be classified in three groups: (1) miniaturization, (2) multi-angle evaluation, and (3) location and type of use.

1. *Miniaturization.* Many manufacturers now supply portable spectrophotometers and colorimeters that provide small size and light weight. Many are battery operated for full portability; others may use fiber-optics probes to separate the measuring head from the remainder of the instrument. In many, the precision is good, but limitations related to measurement geometry may increase bias. If very small illuminated and viewed areas are used, there may be an advantage in that smaller portions of samples can be measured, but averaging of multiple measurements (see ASTM E 1345) may be required to obtain representative values for nonuniform samples.
2. *Multi-Angle Evaluation.* Several manufacturers now supply instruments with multi-angle geometry for the measurement of goniochromatic samples, such as those containing metal flake or pearlescent pigments. For research in this field, a goniospectrophotometer is required. For quality control, however, use of one angle of illumination with several angles of view may suffice. As noted earlier under **Spectrophotometers**, the selection of illuminating and viewing angles has not yet been standardized.
3. *Location and Type of Use.* In earlier times, production samples were taken to a quality-control laboratory for evaluation. This procedure is still desirable in some instances to permit control of such variables as ambient light, temperature and humidity, and atmospheric contamination, but today time is being saved by making measurements on the production floor. For continuous processes, on-line instrumentation is finding greater use. In addition, color measurement and computer-aided color matching (see later in

this chapter under **Instrumental and Computer-Aided Color Matching**) are today finding extensive use at point-of-purchase locations such as retail paint stores.

COLOR DIFFERENCE EVALUATION FOR COLOR CONTROL

The control of the color of industrial paint products may be aided by use of the results of color measurement, as described in the last section. The instruments provide color coordinates of sample and standard from which accurate measures of color difference may be derived. These data can also be used to establish color tolerances. Of course, color differences may also be judged visually, and several ASTM standards address this topic: ASTM Practice for Visual Estimation of Color Differences (D 1729), ASTM Test Method for Evaluation of Visual Color Difference With a Gray Scale (D 2616), and ASTM Guide to the Selection, Evaluation, and Training of Observers (E 1499). This guide also describes materials and methods for the testing and evaluation of the observer's color vision.

Color-Difference Calculations

In the 1931 and 1964 CIE systems, equal distances in different parts of color space do not represent equally perceived color differences. Although many proposals for more uniform color spaces have been made, an ideally uniform space has not been and may not ever be devised. However, modern color-measuring instruments compute sets of color coordinates that correlate better with perceived color differences than do CIE tristimulus values.

Among the many modifications of CIE tristimulus values that have been proposed for more uniform color spaces, those proposed by Hunter [*29*], MacAdam [*38–40*], and the CIE [*12*] are preferred for use in the paint industry and are given in ASTM Test Method for Calculation of Color Differences from Instrumentally Measured Color Coordinates (D 2244). The most widely used of these is the CIE 1976 $L^*a^*b^*$ (CIELAB) space discussed earlier in the subsection entitled **Uniform Color Spaces**. Omitting subscripts *ab* throughout for convenience, the total CIELAB color difference, ΔE^*, is given by

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

where, for example, $\Delta L^* = L^*_{\text{TRIAL}} - L^*_{\text{STANDARD}}$. It is convenient to express ΔE^* in terms of differences in the Munsell-type coordinates hue, chroma, and lightness, but the hue angle h defined earlier in the subsection entitled **Uniform Color Spaces** does not have the same dimensions and scaling as chroma C^* and lightness L^*. Instead of using h, it is necessary to define CIELAB hue difference ΔH^* to combine with ΔC^* and ΔL^*

$$\Delta H^* = [(\Delta E^*)^2 - (\Delta C^*)^2 - (\Delta L^*)^2]^{1/2}$$

Then

$$\Delta E^* = [(\Delta H^*)^2 + (\Delta C^*)^2 + (\Delta L^*)^2]^{1/2}$$

Alternative equations for determining ΔH^* and its sign have been described [*41*]. The unit of CIELAB color difference is two to three times the just perceptible color difference.

In the use of color differences, it is important to examine the components of the color difference, such as ΔL^*, Δa^*, and Δb^*, or ΔL^*, ΔC^*, and ΔH^*, as well as ΔE^* itself. The magnitudes and signs of these components can provide valuable information on remedial action needed to bring a production batch on shade.

The interpretation of measured color differences becomes more complex when the specimens are goniochromatic and measurements are made at several combinations of illuminating and viewing angles. The quantitative meaning of color differences as the angles change has not yet been thoroughly studied.

Since the adoption of the CIELAB equations and their inclusion in ASTM D 2244, a number of new color-difference equations have been developed. One of these, known as the CMC (l:*c*) equation [*42,43*], is a modification of CIELAB that has improved uniformity of visual perception of its color differences. It will be included in an "ASTM Guide to the Selection and Use of Color-Difference Equations" (under development).

Color Tolerances

A valuable means of recording the experience gained in the production of a given color is through the use of color tolerances, expressed as numerical limits to ΔE^* and its components or as color-tolerance charts. Because no color space is entirely uniform and industrial color tolerances are often based on acceptability considerations between buyer and seller, not perceptibility, color differences should be used only as a guide until enough experience has been accumulated for each color to allow specification of a tolerance limit.

Tolerance Charts

Color-tolerance charts are usually enlarged sections of a nearly visually equally spaced diagram, such as the CIELAB a^*, b^* diagram. A color-tolerance chart is set up with the coordinates of the standard at the center, and the differences Δa^* and Δb^* of production batches are entered as they are made (Fig. 18*a*). The process is described in ASTM Practice for Establishing Color and Gloss Tolerance (D 3134). As experience is gained, it should be possible to draw a tolerance-limit curve enclosing most, if not all, of the acceptable batches and excluding most, if not all, of the unacceptable batches. Because no known diagram is perfectly visually uniform, the tolerance limit figure may not be a circle or an ellipse and may not be centered on the location of the standard.

Lightness differences between the standard and batch must also be taken into account. This can be done by use of a separate tolerance for ΔL^*, but better practice is to use a second chart (Fig. 18*b*), in which ΔL^* is plotted against either Δa^* or Δb^*, depending on the data. The batch readings should fall within the tolerance figure on both charts.

It must be emphasized that the final criterion for acceptance of a color is always its visual appearance, to which instrumental measurements, color differences, and tolerance

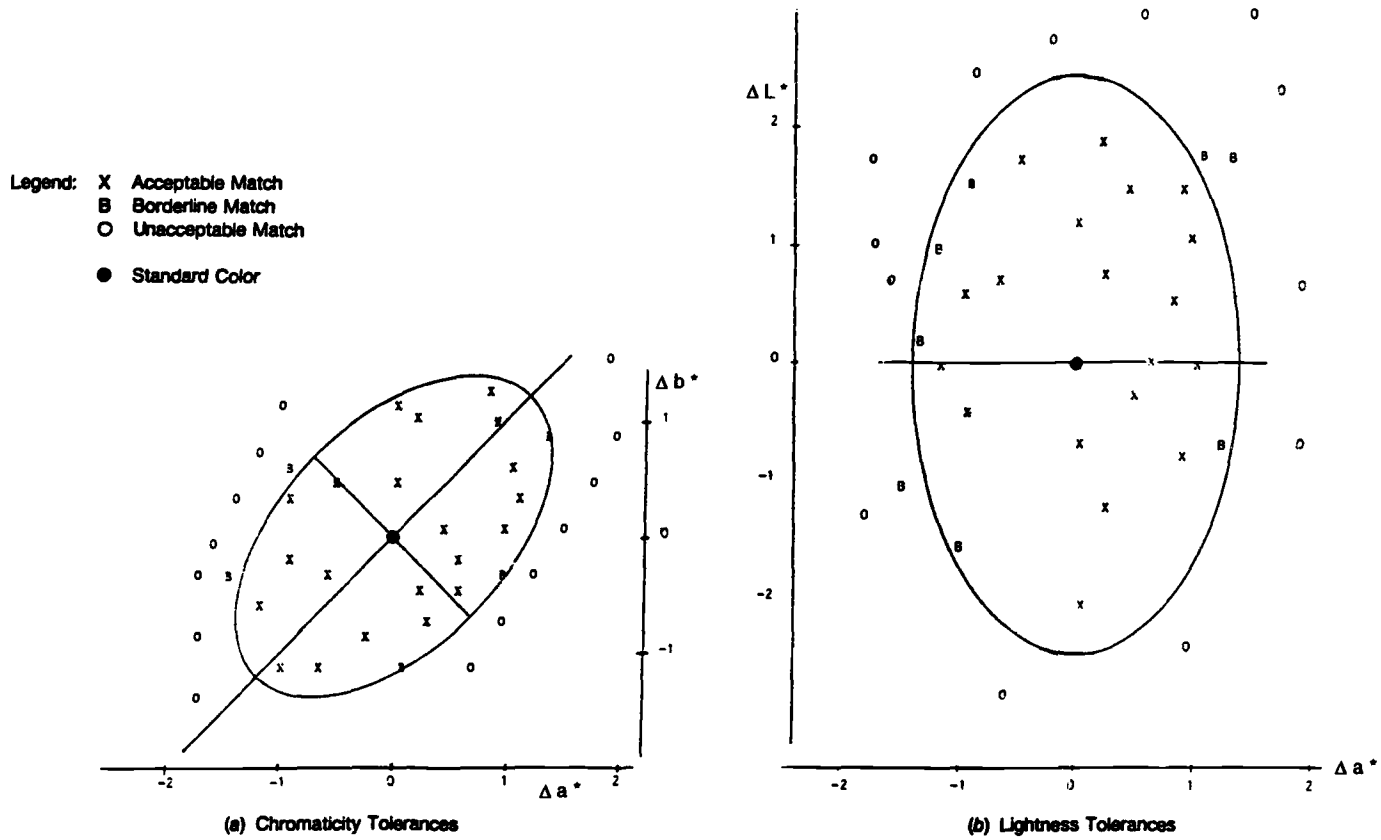

FIG. 18–Color tolerance charts plotted in the CIELAB system: (*a*) chromaticity tolerance figure on a Δa^*, Δb^* diagram; (*b*) lightness tolerance figure on a ΔL^*, Δa^* diagram. In this case, a plot of ΔL^* versus Δb^* would have served as well. (Based on ASTM D 3134.)

charts provide only clues. Instrument malfunctions, miscalibrations, miscalculations, and operator errors can be revealed only by use of confirming visual observations.

Indices of Metamerism

Another important use of color-difference equations is to quantify indices of metamerism as an aid in reducing this defect between standard and batch. The CIE [*12,44*] has recommended that indices of metamerism be calculated as the color differences between two samples that match under a standard illuminant or to a standard observer when measured for a test illuminant or a test observer. For illuminant metamerism, the standard illuminant is usually daylight, and the second can be selected by the user. For observer metamerism, the standard observer is either the CIE 1931 or 1964 observer, and a corresponding second "standard deviate" observer is provided [*44*] based on the range of normal color vision found in the human population.

COLOR MIXING

Additive Mixing of Lights

When a white card is illuminated, its apparent color is the color of the incident light; a red light, for example, makes it appear red. Three colored lights (red, green, and blue), if carefully chosen, would, when placed to overlap on the same area of the card, produce white again (Fig. 19). In this area, the reflected lights from the three sources add together. These three lights are called the additive primaries. By adjusting the intensities of each of the three lights, a wide range of colors can be produced.

The procedure just described can provide an analytical tool for color measurement. If an adjacent spot on the white card is illuminated by light of an unknown color, it could be matched visually, in principle, with the three-light combination by adjusting their intensities. This is the basis for color matching by addition of lights. The additive principle is used to produce the colors in television [*45*].

The analytical device described above is also a simple version of the visual colorimeter used to generate the tristimulus values of the spectrum colors that form the basis for the CIE Standard Observers (see earlier in this chapter under **CIE Standard Observers**). At each wavelength, the total light reflected is the sum of the power reflected from each of the three primary lights. Since tristimulus values are obtained by adding such sums across the spectrum, they too are produced by additive mixing. It is not necessary to know the spectral nature of the additive primaries to predict the resulting colors.

Subtractive Mixing in Transparent Films

Now consider the light falling on a white card after passing through a film that contains three transparent colorants, yel-

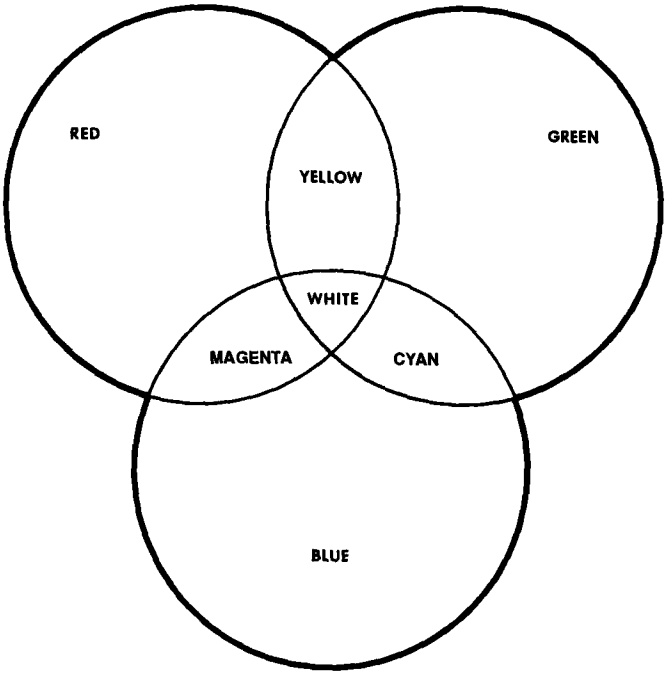

FIG. 19–Representation of the additive mixing of colored lights showing the additive primaries red, green, and blue forming the mixture colors yellow, cyan, and magenta where the primaries overlap in pairs and white where all three overlap.

low, cyan (blue-green), and magenta (red-purple). This might be the situation with a free-standing transparent plastic film, for example. If the three colorants were ideally chosen, all the light would be absorbed when all three were present, and the result would be black (Fig. 20). These three colorants are called the subtractive primaries. If varying quantities of them were combined in subtractive mixing, a wide variety of colors could be produced. However, these mixture colors cannot be predicted from the colors of the primaries alone, as in the additive mixing described above. One must also know their spectral character and compute, wavelength by wavelength, how much light is removed by each primary through absorption, using the well-known Beer's law relationship. From what is not absorbed, tristimulus values can be calculated in the usual way.

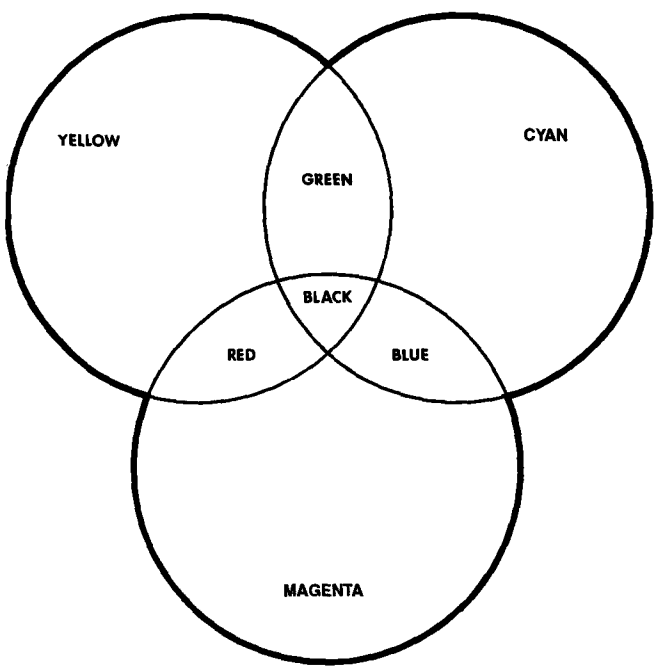

FIG. 20–Representation of the subtractive color mixing of transparent colorants showing the subtractive primaries yellow, cyan, and magenta forming the mixture colors green, blue, and red where the primaries are mixed in pairs and black where all three are mixed together.

Pigment Mixing

Most paint films contain, in addition to three colored pigments (one of which may be black), a white pigment used as an opacifier. The mixing of colors produced in this way is more complex than simple subtractive mixing in transparent films because of the scattering of light caused by the white pigment (and by opaque colored pigments as well). Again, it is necessary to know the spectral character of all the colorants present. The Beer's law calculation of the transparent case is replaced by the Kubelka-Munk relation: For opaque films, as is usually the case in the paint industry, this is a simple equation relating the reflectance $R(\lambda)$ of the film at each wavelength to the ratio of two constants describing what happens to the light in the film

$$K(\lambda)/S(\lambda) = [1 - R(\lambda)]^2/2R(\lambda)$$

where $K(\lambda)$ is the Kubelka-Munk absorption coefficient, and $S(\lambda)$ is the Kubelka-Munk scattering coefficient. Here $R(\lambda)$ must be expressed as a fraction, not the usual percentage. The quantities $K(\lambda)$ and $S(\lambda)$ refer to the mixture of pigments in the paint film. These are calculated by adding the separate contributions of each pigment, using its $K(\lambda)$ and $S(\lambda)$ weighted by its concentration C in the mixture

$$\frac{K(\lambda)_{\text{MIXTURE}}}{S(\lambda)_{\text{MIXTURE}}} = \frac{C_1K_1(\lambda) + C_2K_2(\lambda) + \cdots}{C_1S_1(\lambda) + C_2S_2(\lambda) + \cdots}$$

where there are as many terms as there are pigments used. These equations form the basis for computer color matching described in the next section.

COLOR MATCHING

One of the major objectives of industrial coloring is to match the color a customer wants. Whether this is done visually or with the aid of instruments and computers is often a matter of work load and economics. Therefore we address both visual and instrumental matching. In either case, a major objective of color matching in paint systems is the formulation of a nonmetameric match to a given paint sample. The difference in spectral character of the samples of a metameric pair is the property determining their metamerism, and achieving a nonmetameric match places several requirements on the formulation.

First, the same pigments must be used. This requires identification of the pigments in the sample to be matched. Second, the pigments must be used in the same resin system since the spectral properties of pigments can depend upon

the choice of binder. Finally, the same degree of dispersion must be achieved since the absorption and scattering properties of pigments that determine their spectral character change with degree of dispersion. This usually means that the same method of dispersion must be used.

Visual Color Matching

The selection of visual color matchers should be made with great care, and reference should be made to ASTM E 1499 for details of how to make the selection, test the color vision of the candidates, and train them in making visual judgments.

Beyond this there is no substitute for the experience of the visual color matcher. He or she must learn the skill by practice. This should include becoming familiar with one of the better color order systems and atlases and learning how to use it, coupled with knowledge of the behavior of the paint system and pigments available, to predict the colors that result from mixing them under carefully controlled conditions. Careful record keeping to document the results is essential. Visual methods of recognizing and controlling metamerism have been described [*46,47*]. These require no more than knowledge of the behavior in mixtures of the pigments used and a good color matching booth (see earlier in this chapter under **Color Matching Booths**).

Instrumental and Computer-Aided Color Matching

The importance of eliminating metamerism dictates that, for a color matching aid, the instrument of choice is clearly the spectrophotometer. Display of the spectral curves of samples, and the computer-aided color-matching operations that lead to spectral curve shapes minimizing metamerism, cannot be achieved by the use of other types of instruments. The spectrophotometer can also be used in a simple but powerful method of organic pigment identification [*48*] based on extraction of the pigments into solution followed by spectrophotometry. This can be an important aid to selecting the same pigmentation for the match as was used in the standard.

Many modern color-measuring spectrophotometers can be obtained with computer software for color matching. Most of these systems work very well, but it must be emphasized that the investment in building up the database that is essential for their use, and in taking all the steps necessary to bring the coloring process under precise control, is not a small one; only when large numbers of colors must be matched on a daily basis can the cost of setting up and maintaining such a system be justified.

The details of how computer color matching works are beyond the scope of this chapter. In summary, most systems call for measurement of the sample to put its spectral data into the computer. These data are matched at each of (usually) 16 wavelengths across the spectrum by Kubelka-Munk-type calculations (see earlier under **Pigment Mixing**), using stored values of $K(\lambda)$ and $S(\lambda)$ for the useful pigments in the product line. The results are the pigment concentrations in the formulation. Several formulations arising from mixing different pigments are usually produced. Additional calculations of metamerism indices and pigment costs allow the selection of the most suitable results.

Computer color matching has been discussed in a book [*49*], and some textbooks [*1,2,5,50,51*] provide useful summaries. The underlying Kubelka-Munk theory, applied to paint systems, has been the subject of several articles [*52–55*] directed to paint colorists. More complex theory appears to be needed only in special cases, such as matching automotive paints containing metal flake or pearlescent pigments. The development of such theories is still in its early stages.

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41

Gloss

by Harry K. Hammond III[1] *and Gabriele Kigle-Boeckler*[2]

THE APPEARANCE OF AN OBJECT or material can be described by its color and gloss characteristics. Like color, gloss can be subdivided into several aspects depending on viewing conditions. In 1937, Richard Hunter identified five aspects of gloss [*1*] and the functions of reflectance by which they could be evaluated. Latest studies by K. Lex [*2*] expanded Hunter's gloss terms and divided them into two groups. One group is based on visual observation with the eye focused on the surface of the material (Fig. 1). For the other group, the eye is focused on the image of the object reflected by the material (Fig. 2). However, experience has shown that no single objective measurement of gloss will provide perfect correlation with the integrated subjective appraisal of glossiness that the eye so quickly renders. For this reason, the gloss evaluation requirement of an object or material should first be examined and the most useful gloss measurement aspects then selected.

ASPECTS OF GLOSS AND THEIR DEFINITION

The simple term "gloss" is defined in an ASTM standard, Terminology of Appearance (E 284) [*3*] as "angular selectivity of reflectance, involving surface-reflected light, responsible for the degree to which reflected highlights or images of objects may be seen as superimposed on a surface." To indicate specific types of "angular selectivity," such as those involving specular gloss, sheen, or haze and to illustrate the difference between an evaluation where the focus is on the surface and one where the focus is on the reflected image, the complexity of the phenomenon "gloss" is illustrated in Fig. 3.

By focusing on the reflected image of an object, an observer obtains information on how distinctly the object is reflected by the surface. A reflected light source may appear brilliant or diffuse depending on the specular gloss of the surface. The outline of a reflected object may appear distinct or blurred depending on image clarity. A halo surrounding the image of the reflected object is an indication of haze. Focusing on the surface of an object provides information on the size, depth, and shape of surface structures contributing to such things as waviness or directionality of brush marks.

[1]Consulting scientist, BYK-Gardner USA, 2435 Linden Lane, Silver Spring, MD 20910.
[2]Technical marketing manager, gloss, BYK-Gardener USA, 2435 Linden Lane, Silver Spring, MD 20910.

Specular Gloss

Specular gloss is defined in ASTM E 284 [*3*] as the "ratio of flux reflected in specular direction to incident flux for a specified angle of incidence and source and receptor angular apertures" (Fig. 4). This aspect of gloss has been measured most frequently because it is the one for which an instrument is most easily constructed. In practice the divergence angles of source and receptor are precisely specified in ASTM Test Method for Specular Gloss (D 523) [*4*] as are the directional angles of incidence and reflection. Tolerances are specified for all angles. For simplicity, glossmeter geometries are identified by reference to the incidence angles, most frequently 20, 60, and 85°. However, the associated source and receptor aperture angles and their tolerances play a vital role in determining the reproducibility of instrument readings.

Sheen

Sheen is defined in ASTM E 284 [*3*] as "the specular gloss at a large angle of incidence for an otherwise matte specimen." The usual angle for sheen measurement is 85° from the perpendicular to the specimen. This is about the maximum angle that can be used without encountering difficulty in positioning the optics to illuminate and view the specimen at near-grazing angles.

Haze

Haze in coating films is often designated "reflection haze" because in plastics there is encountered a near-forward scattering in transmission that is designated transmission haze. ASTM E 284 [*3*] defines haze in reflection as "percent of reflected light scattered by a specimen having a glossy surface so that its direction deviates more than a specified angle from the direction of specular reflection."

Image Clarity

This aspect of gloss has often been referred to as "distinctness of image." It is essentially independent of haze or change in specular gloss. ASTM E 284 [*3*] defines distinctness-of-image gloss as "the aspect of gloss characterized by the sharpness of images of objects produced by reflection at a surface." During visual observation, the sharpness of the light-dark edge of a reflected object can be observed. Image

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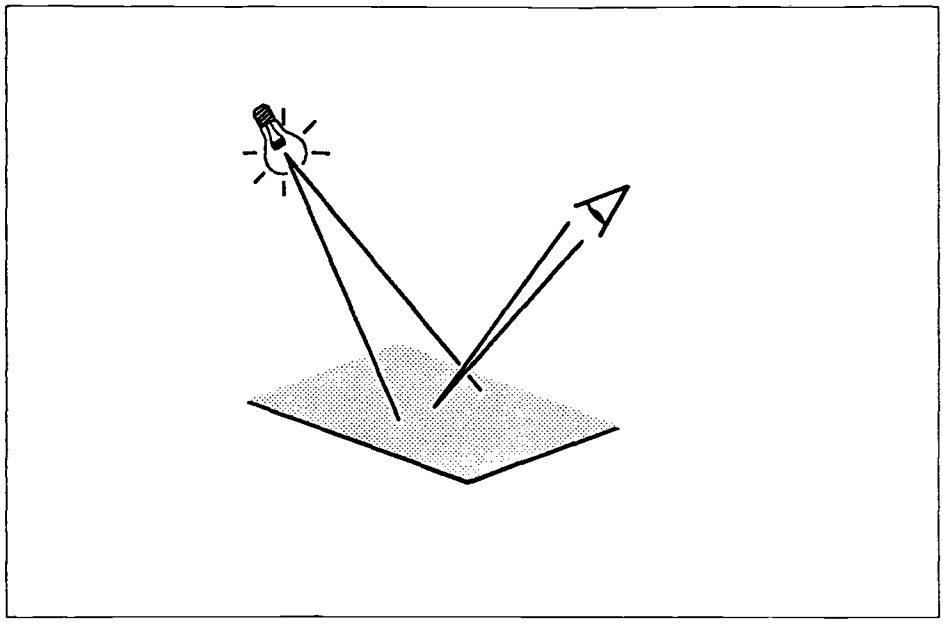

FIG. 1–Observer focuses on the image of reflected object.

clarity is a critical parameter of glossy surfaces having only small amounts of waviness.

Waviness

One obvious type of waviness is designated "orange peel." ASTM E 284 [3] defines orange peel as "the appearance of irregularity of a surface resembling the skin of an orange." A surface may be described as exhibiting orange peel when it has many small indentations that are perceived as a pattern of both highlighted and non-highlighted areas. This pattern is interpreted by an observer as a three-dimensional structure of hills and valleys.

Directionality

ASTM E 284 [3] defines directionality, perceived, as "the degree to which the appearance of a surface changes as the

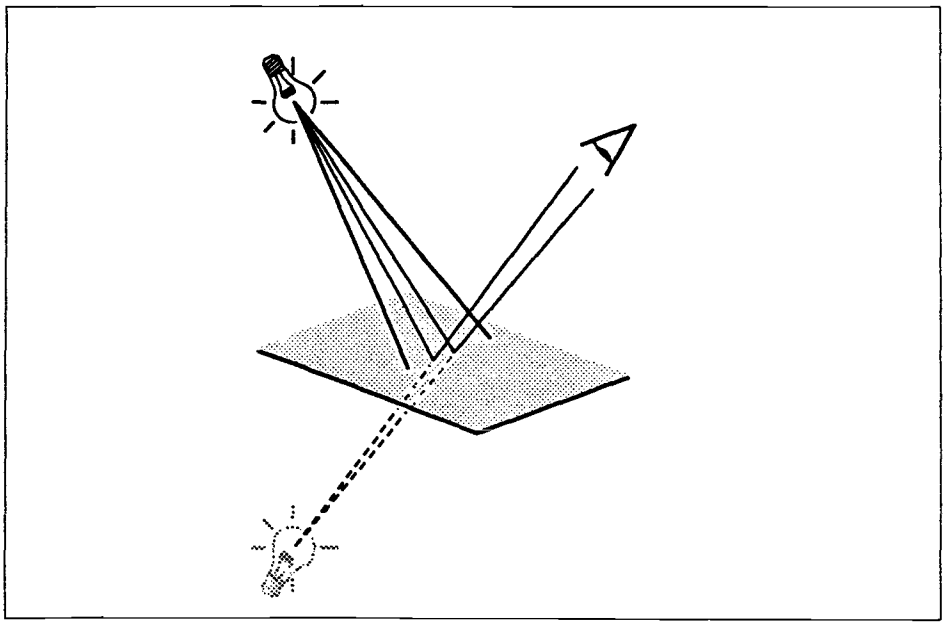

FIG. 2–Observer focuses on the illuminated surface of object.

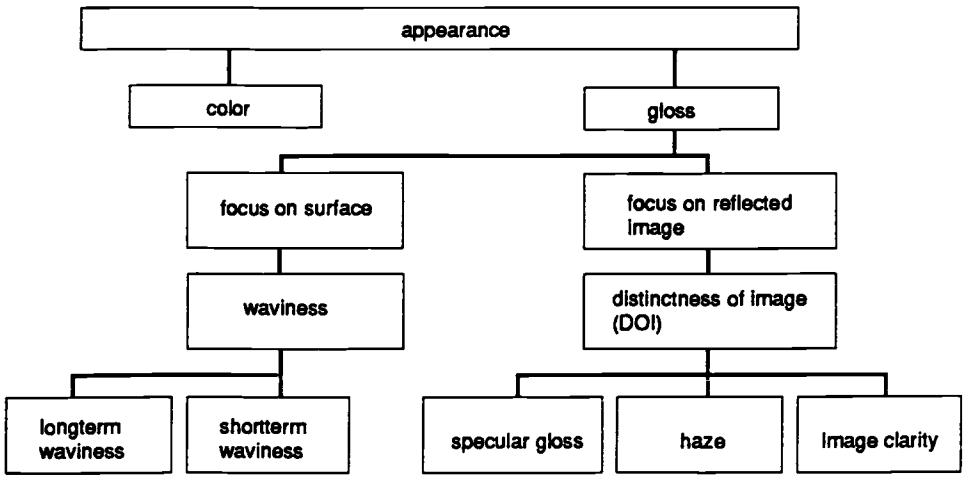

FIG. 3–Flow chart depicting relationships of various appearance characteristics.

surface is rotated in its own plane, under fixed conditions of illumination and viewing." A surface exhibits directionality when specular gloss measurements are a function of the direction for which measurements are made. When paint is applied by brushing in one direction, the brush marks can cause the surface to have a directional characteristic. Metallic materials frequently exhibit directionality when the surface is polished in one direction.

VISUAL GLOSS EVALUATION

Early investigations of gloss were carried out by observing differences in the characteristics of images reflected in the surfaces of specimens. In 1932, the Detroit Paint and Varnish Production Club [5] reported on investigations carried out with their distinctness-of-image gloss comparator. In 1936, Hunter [6] reported an investigation where reflected images of a target pattern were observed.

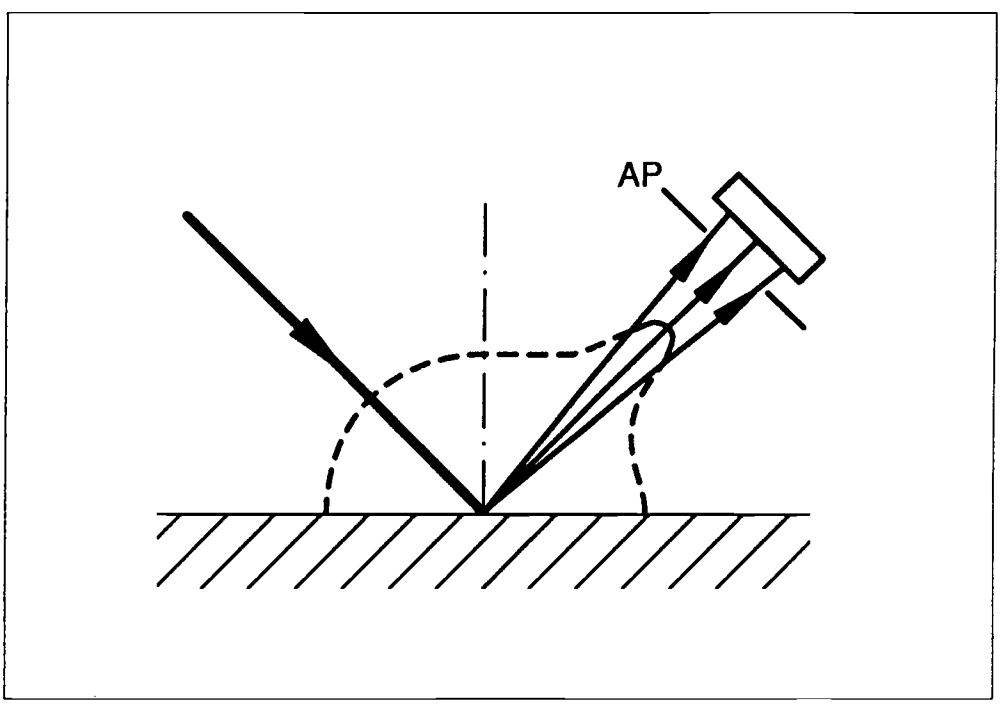

FIG. 4–Reflected light flux distribution from a semigloss surface is depicted by a broken curve. Three lines are shown proceeding from the specimen surface. The center one depicts the specular direction, the image of a ray reflected from a mirror-like surface. The two other rays represent the range of angles passing through the aperture (AP) to the detector (shown as a rectangle).

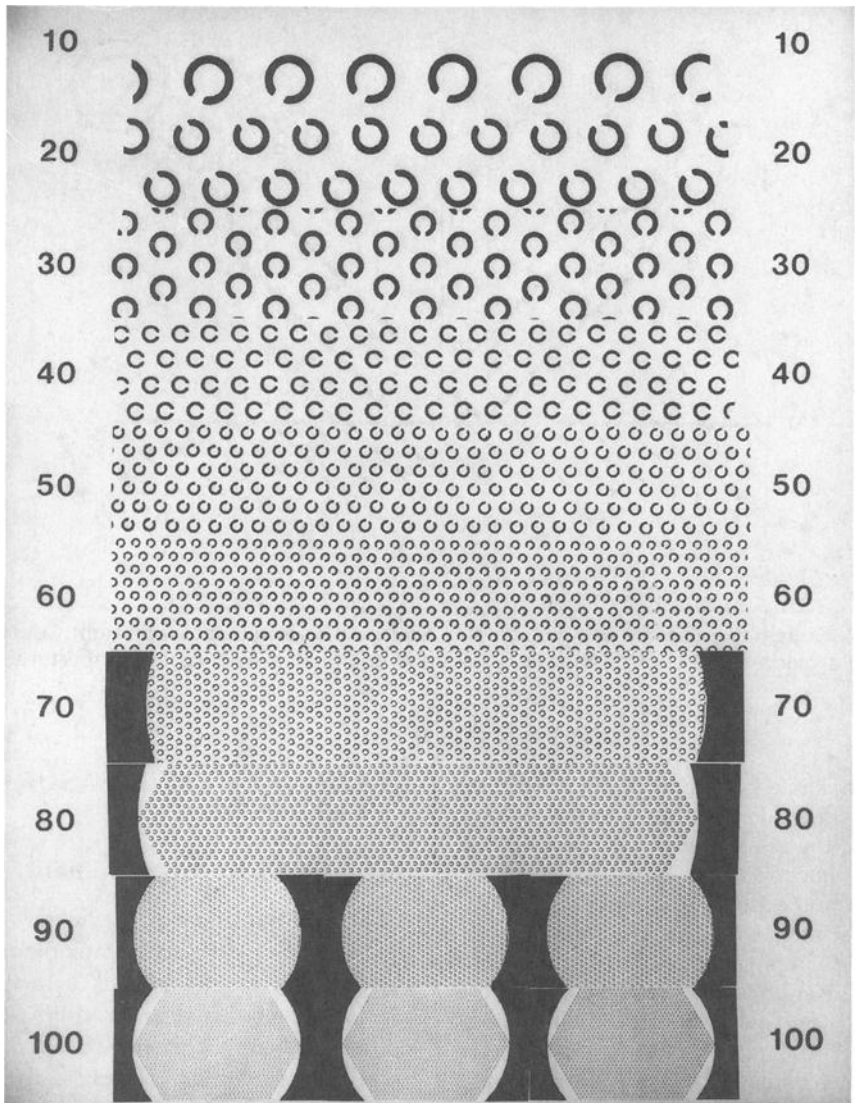

FIG. 5–"Landolt Rings." Broken rings of bvarious sizes are used to provide a scale for visual evaluation of the distinctness of surface-reflected images.[3]

Only in comparatively recent times has there been a major effort to investigate visual scaling of gloss and to endeavor to develop correlation between visual and instrumental measurements. O'Donnell did a doctoral thesis on visual gloss scaling at Rensselear Polytechnic Institute, Troy, New York. Results were first presented, in part, at an ASTM Symposium in 1984 [*7*] and more fully in a journal article in 1987 [*8*].

Development of a Documentary Standard

In 1990, ASTM Committee D-1 on Paint and Related Coatings and Materials published ASTM Method for Visual Evaluation of Gloss Differences Between Surfaces of Similar Appearance (D 4449) [*9*] for making visual evaluations of gloss between surfaces of similar appearance. It uses two types of light sources. One source consists of a tubular fluorescent desk lamp modified by placing a matte-black reflecting material behind the tubes and a coarse wire-mesh screen in front. The directions of illumination and view can be adjusted to be 20, 60, or 85° as desired for comparing specimens having high gloss, intermediate gloss, or sheen. The other light source is a clear-bulb incandescent lamp. Light from the selected source illuminates the specimens at the chosen angle. The sharpness of reflected images permits a subjective comparison of the relative gloss of similar surfaces.

Use of Landolt Rings

Landolt rings have been used by ophthamologists to evaluate visual acuity for nearly a hundred years [*10*]. The test

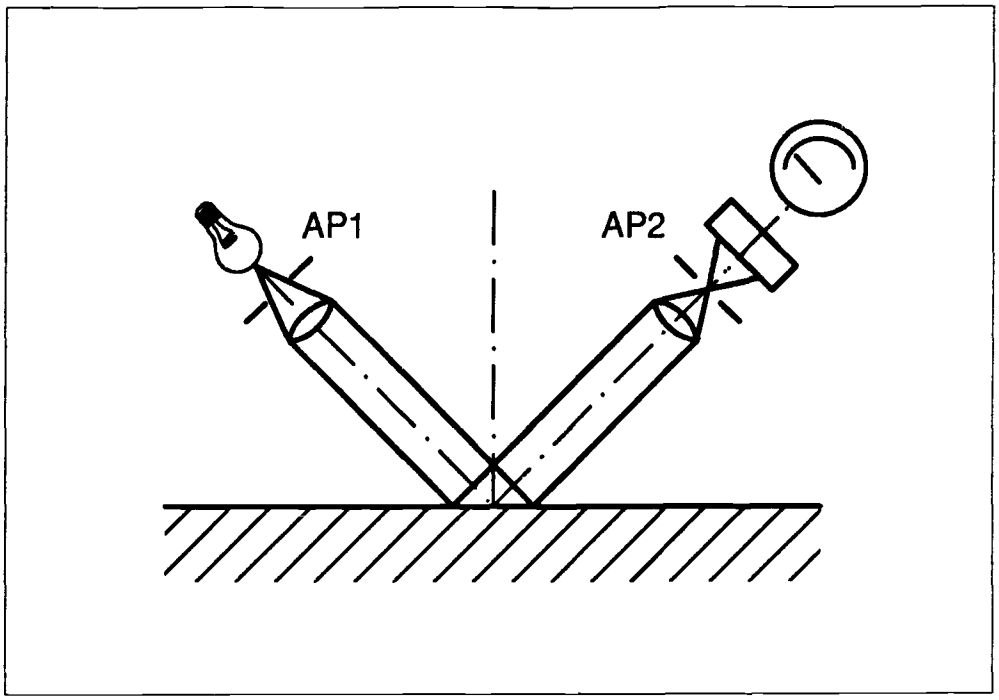

FIG. 6—Schematic diagram of a gloss meter. Source is on left, detector on right. Lenses are used to provide beam control. Source aperture is designated AP1, receptor aperture AP2.

consists of locating the gaps in a graduated series of sizes of incomplete rings whose radial thickness and gap are equal to one fifth the diameter of the ring. For gloss evaluation of trans-illuminated rings, reflections are viewed on mylar. Rings have different sizes and different gap orientations. An image-gloss scale is associated with the different sizes of rings. An image-gloss scale ranging from 10 to 100 in steps of ten was established for eleven sizes of rings from the largest to the smallest. The development of the scale is not documented, but it ostensibility took place in the General Motors Automotive Division about January 1977. Visual observers select the smallest size of ring for which they can call the gap orientation correctly. The numerical size of the rings is used as an inverse index of distinctness-of-image gloss (Fig. 5). ASTM has not published a method for visually evaluating distinctness-of-image gloss by using Landolt rings, but equipment for this purpose is available.[3]

Visual Evaluation of Orange Peel

The automotive industry established a physical standard for orange peel consisting of ten high-gloss panels with various degrees of orange peel structure.[4] The panels are visually ranked from 1 to 10 with Panel Number 1 depicting very pronounced orange peel and Panel Number 10 illustrating no orange peel. The visual observer can use these panels as a supportive tool to evaluate degree of orange peel.

[3]Apparatus for evaluating distinctness of image using Landolt rings, available from Paul N. Gardner Co., Pompano Beach, FL.

[4]Set of orange-peel panels can be obtained from Advanced Coatings Technology, 273 Industrial Dr., Hillsdale, MI 49242.

INSTRUMENTAL MEASUREMENT TECHNIQUES

Specular Gloss Measurement

The design of many gloss meters is based on the precise measurement of the specular component of reflected light. A light source, usually a small filament incandescent lamp, is placed at the focal point of a collimating lens. The axis of the collimated beam is set to the desired angle of illumination. A receptor lens with an aperture in the focal plane followed by an illumination detector completes the basic optical design (Fig. 6 and Fig. 7). The size of the receptor aperture and the size of the source image in that aperture are the elements that complete the optics and that determine the high, low, and intermediate gloss scale readings. The specular angle largely determines the magnitude of the reflected light. However, the tolerances assigned to the source and receptor apertures are what determine the accuracy and reproducibility of measurements made with instruments having the same angles of illumination and view.

Periodic calibration or verification of instrument performance requires the use of calibrated gloss standards. For permanence they should be made of glass or ceramic material. ASTM D 523 recommends the use of a primary standard of polished black glass of known refractive index for which the Fresnel (specular) reflectance [*11*] has been computed for the angle of incidence of the geometry for which the instrument is designed. Since about 1990, national standardizing laboratories have preferred a primary reference stan-

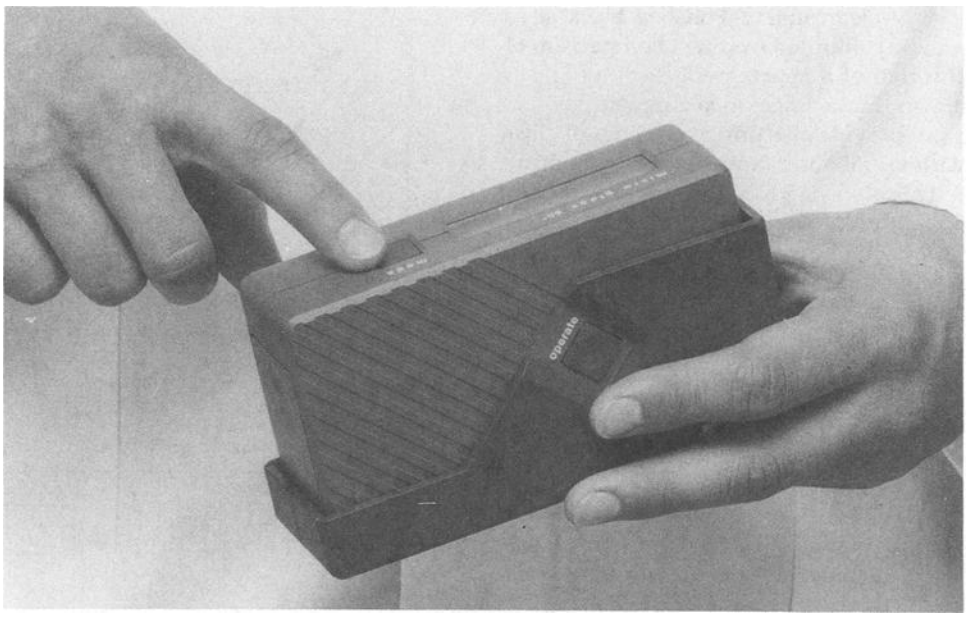

FIG. 7–Photograph of a modern miniature glossmeter. Note size of the hand holding the instrument.[5]

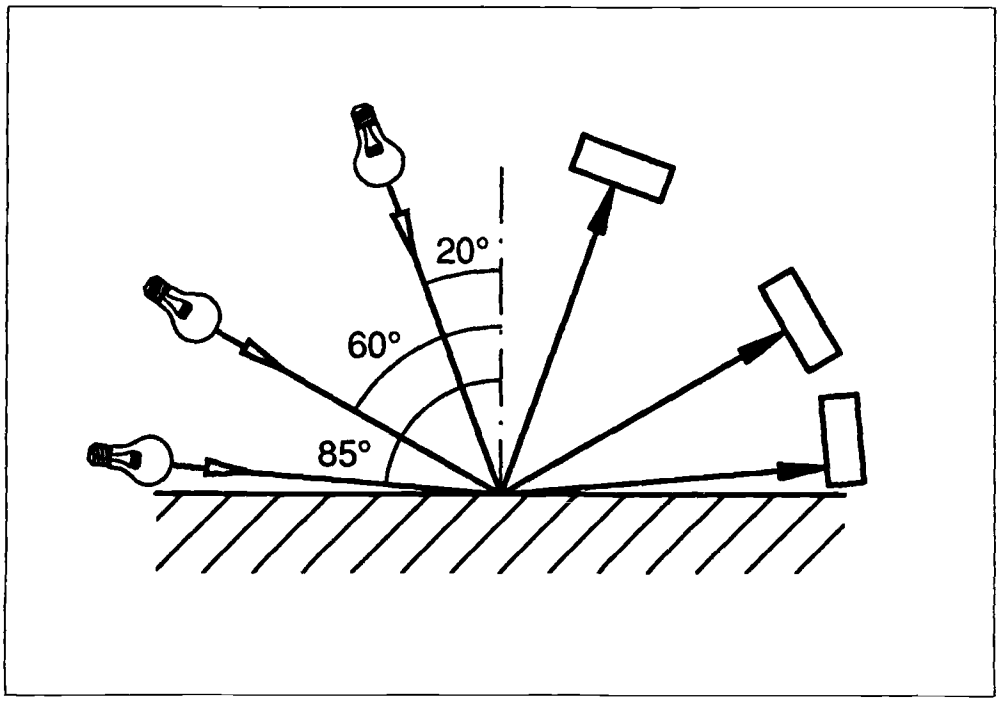

FIG. 8–Diagram depicting the positions of source and receptor for the three geometries of ASTM D 523.

[5]Apparatus designated "micro-TRI-gloss," available from BYK-Gardner USA, Silver Spring, MD.

dard made of a wedge of clear quartz. Polished black glass working standards can be calibrated by direct comparison of their reflectances with that of a quartz wedge.

Experience has shown that a single measurement geometry, such as 60°, may not provide instrument readings of gloss that correlate well with visual observations when comparing different gloss levels. This is why ASTM D 523 [*4*] provides for measurement at three different angles of incidence, namely 20, 60, and 85° (Fig. 8). Each of the three geometries uses the same source aperture, but a different receptor aperture. The choice of geometry depends on whether one is: (1) making a general evaluation of gloss, (2) comparing high-gloss finishes or (3) evaluating low-gloss specimens for sheen. ASTM D 523 [*4*] states that the 60° geometry is used for intercomparing most specimens and for determining when the 20 or 85° geometry may be more applicable. The 20° geometry is advantageous for comparing specimens having 60° gloss values higher than 70. The 85° geometry is used for comparing specimens for sheen or near-grazing shininess. It is most frequently applied when specimens have 60° gloss values lower than 10.

The ASTM documentary gloss standard originally published in 1939 contained only the 60° geometry [*12*]. The desirability of using an auxiliary geometry of 85° for sheen evaluation was recognized shortly afterward. However, the use of another geometry with smaller angles of incidence and view, such as 20°, and a smaller receptor aperture to provide improved differentiation of high-gloss finishes was not published until 1947 [*13*]. The three geometries, 20, 60, and 85°, were originally published as separate ASTM standards. In 1953, ASTM D 523 was revised to incorporate all three geometries, and it still does.

Meanwhile the Paint Committee of the International Organization for Standardization, ISO TC-35, was investigating gloss measurements with various commercial instruments prior to drafting an international standard. A paper documenting what the committee had been doing was published in 1976 by the Chairman of the Gloss Task Group, Dr. Ulrich Zorll [*14*]. In 1978, the ISO Paint Committee published ISO 2813, essentially an international version of ASTM D 523 [*15*]. In keeping with the usual ISO procedure, the standard was made available in English, French, and German.

Instrument manufacturers report that measurement precision, reproducibility, and data-handling capabilities of gloss meters have been improved markedly in recent years. New instruments have been designed that are smaller, more portable, and more convenient to use. Data storage and analysis are frequently included as well as the capability of electronically transferring data to a personal computer [*16,17*].

Goniophotometry

Gonio means angle, and photometer means light; so a goniophotometer is an instrument for measuring the angular distribution of reflected or transmitted light. This type of instrument is used regularly in the research laboratory to investigate the distribution of light flux (Fig. 9). A goniophotometer with appropriate apertures can also be used to provide gloss data for a wide variety of angles and apertures. When goniophotometric measurements are desired,

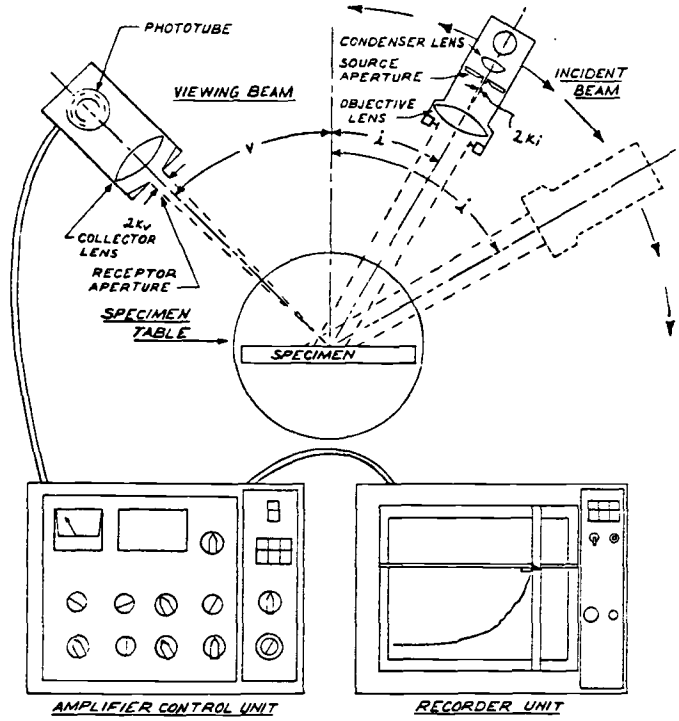

FIG. 9–Schematic diagram of a goniophotometer.

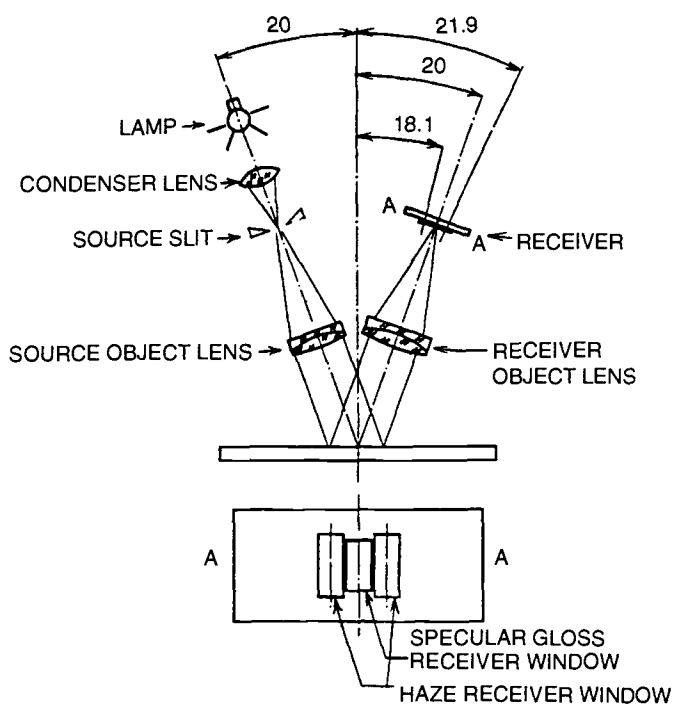

FIG. 10–Schematic diagram of an instrument for reflection haze measurement.

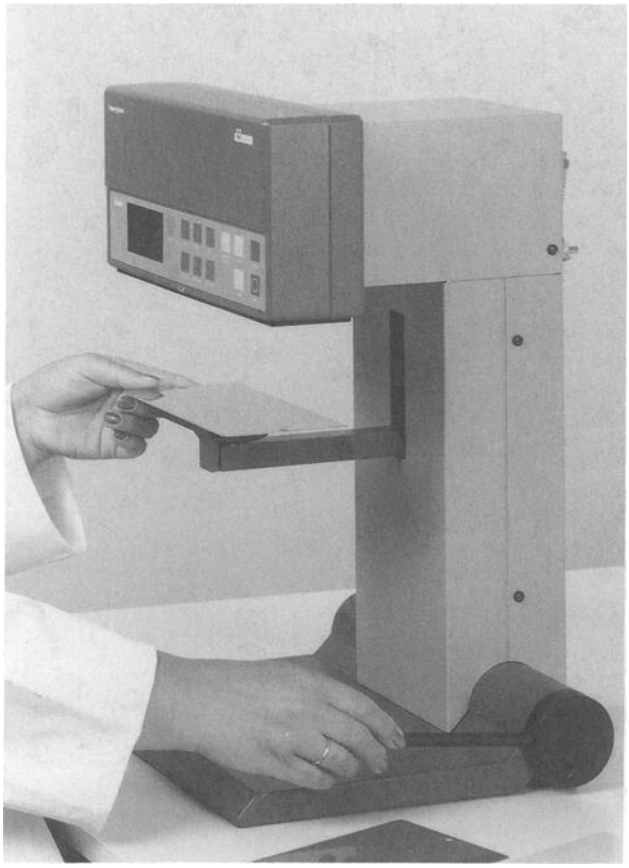

FIG. 11–Photograph of a haze-and-gloss-measuring instrument.[6]

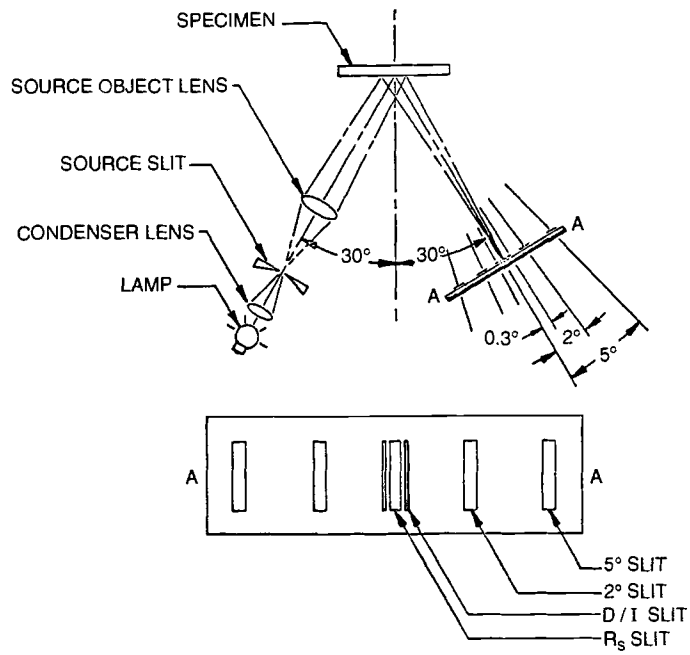

FIG. 12–Schematic diagram of an instrument for image clarity measurement.[7]

reference should be made to ASTM Practice for Goniophotometry of Objects and Materials (E 167) [*18*]. Analysis of goniophotometric curves was treated by Nimeroff [*19*].

Measurement of Reflection Haze

Haze is a gloss parameter that causes a high-gloss surface to appear milky and lighter, thereby losing contrast. When visually evaluating the reflected image of a hazy object, one observes halos around distinct reflection outlines caused by scattered light. Haze can result from various material or process parameters such as degree of dispersion, flocculation, incompatibility of raw materials (pigment-additive-resin) or from poor application procedures. Microscopic irregularities cause small amounts of reflected light to be scattered adjacent to the direction of specular reflection or to modify the refractive index of the material just beneath the surface.

Haze is most often associated with high-gloss surfaces when small amounts of reflected light are scattered in a region 1 to 4° from the direction of specular reflection. Therefore, it is useful to place apertures several degrees wide on each side of the specular receptor aperture (Fig. 10). ASTM Test Methods for Measurement of Gloss of High Gloss Surfaces by Goniophotometry (E 430) [*20*] describes two methods for evaluating reflection haze, one at 20°, another at 30°. An instrument using a 30° angle has been commercially available for more than 15 years.[7] Since about 1992, a 20° laboratory gloss meter has been equipped with auxiliary apertures for haze evaluation, thus permitting measurement of 20° specular gloss and haze with the same instrument (Fig. 11).

Measurement of Image Clarity

A variety of different technologies is commercially available to measure image clarity [*21-24*]. The two most often used principles are: (1) measurement of the contrast in dependence of the wavelength of the transferred sinus wave (fourier-transformation) resulting in a modulation transfer function or (2) evaluation of the steepness of the reflection indicatrix. ASTM E 430 [*20*] describes the design of a commercially available instrument based on the evaluation of the reflection indicatrix (Fig. 12). The instrument illuminates the specimen at a 30° angle and measures the light reflected at 0.3° from the specular angle with an aperture of 0.3° width.

An attempt was made to correlate the surface waviness of coatings with image clarity measurements [*23,25*]. However, different surface profiles provided nearly the same image clarity readings [*21*].

[6]Apparatus designated "haze-gloss," available from BYK-Gardner USA, Silver Spring, MD.

[7]Apparatus designated "Dorigon," available from Hunter Associates Laboratory, Inc., Reston, VA.

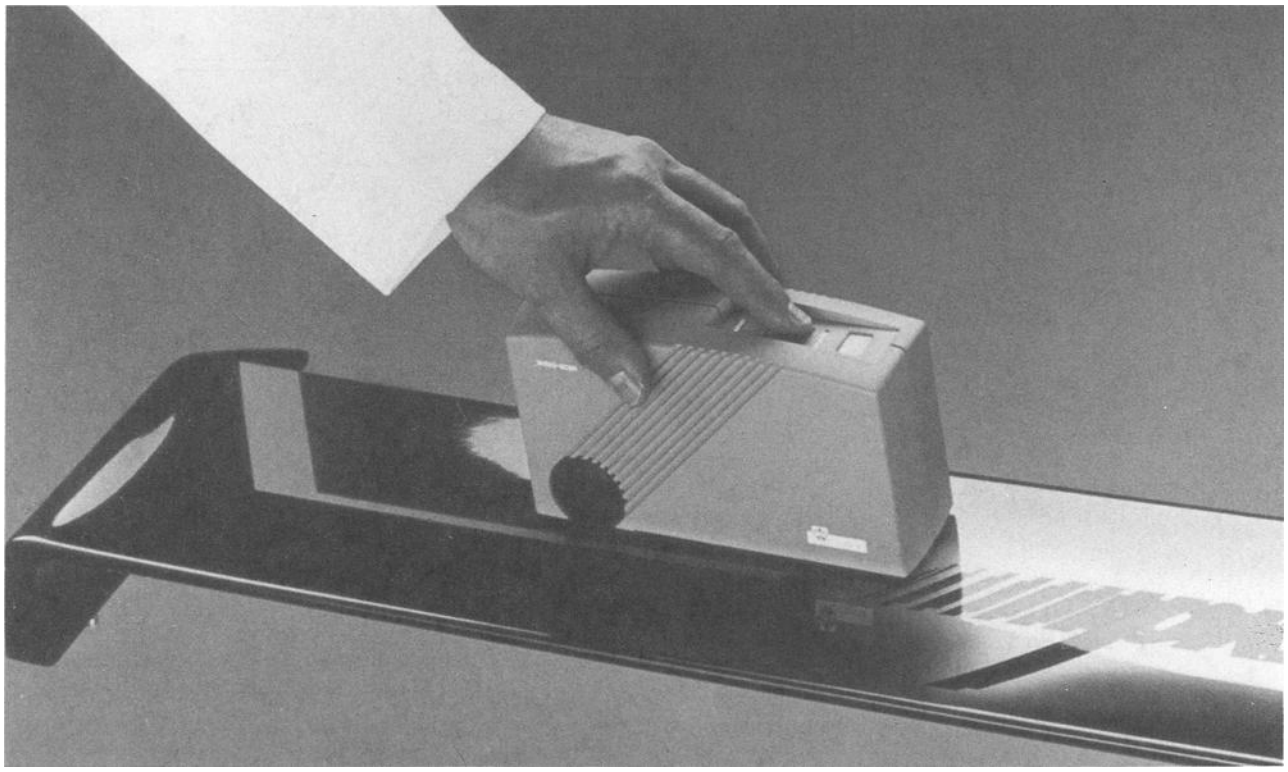

FIG. 13–Photograph of an orange-peel-measuring instrument.[8]

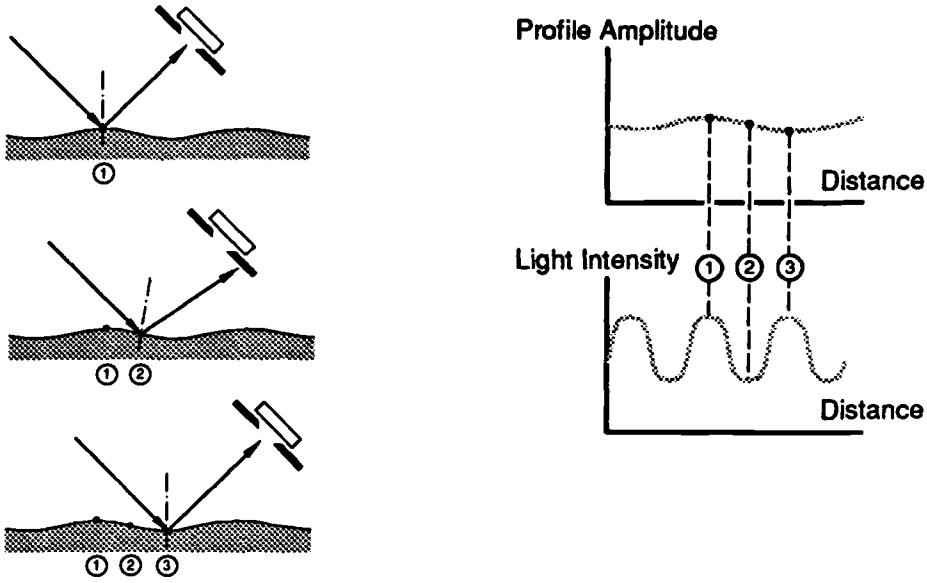

FIG. 14–Schematic diagram of the measurement principle for evaluation of orange peel.

[8]Apparatus designated "wave-scan," available from BYK-Gardner USA, Silver Spring, MD.

Measurement of Waviness (Orange Peel)

The phenomena of waviness is most observable on a glossy surface, a critical appearance phenomena in the automotive industry. Waviness has been evaluated by visual means and by use of a profilometer. The correlation between profilometry measurements and visual perception is satisfactory for surfaces with similar optical properties. The operation of a profilometer, however, is very time consuming and limited to laboratory use. When the eye of an observer is focused on a painted surface, various types of waviness can be identified that involve size, structure, and shape. Variations in process or material parameters can cause differences in surface structure. For example, poor flow or levelling properties of a coating will usually cause a long wave structure often called orange peel. Changes in substrate roughness, on the other hand, will exhibit a shortwave structure of higher frequency. Because waviness is often caused on the production line, it is important to control it there.

After considerable research, an instrument was produced in 1992 that will provide an objective evaluation of waviness [*26*] (Fig. 13).

A diode laser source is used to illuminate the specimen at 60°. The reflected light intensity is evaluated at the specular angle. During the measurement the instrument is moved along the surface for a distance of about 10 cm. The intensity of the reflected light is a maximum when coming from a valley or peak of an orange peel element. The detector receives less light from the slopes (Fig. 14). The human eye cannot resolve the actual heights of the structural elements of a painted surface (2 to 4 μm), but the contrast between light and dark areas provides an impression of depth. The contrast of a surface structure can be expressed by use of the statistical parameter "variance." The final measurement results are divided into a short wave component (structure size between 0.06 and 1 mm) and a long wave component (structure size between 1 and 10 mm) using an electronic filtering procedure. This evaluation reflects the simulation of the visual perception at different distances and permits categorizing structure sizes with their causes.

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42

Hiding Power

by Leonard Schaeffer[1]

1. CONCEPTS, RELATIONSHIPS, TERMINOLOGY

a. Opacity

When light enters a paint film, some or all of it is absorbed or reflected by the film before reaching the substrate, thereby hiding the substrate to a lesser or greater degree. The light that reaches the substrate is partly absorbed by it and partly reflected back in conformance with the substrate's visual pattern. Reflection from the substrate eventually emerges from the film carrying the substrate reflectivity information perceived as visibility or lack thereof and referred to as *hiding*. Opacity may be qualitatively defined as the property of a paint film that enables it to prevent the passage of light and thereby to hide the substrate on which it has been applied. Note that *opacity* is a film property, whereas *hiding power* is a property of the whole paint. *Hiding* is a more general term used frequently to refer to either opacity or hiding power.

b. Light Absorption

If most of the light is absorbed by the film before reaching the substrate, the film is dark in color and hides the substrate well, in which case hiding has been produced by light absorption.

c. Light Scattering

If most of the light entering the film is reflected back and reemerges without having reached the substrate, the film is white or light in color and hides the substrate well. The reflection mechanism of the film involves multiple internal refractions and reflections that scatter the light to produce a net reversal in its direction. Hiding in this case is produced by light scattering.

d. Incomplete Hiding

In all cases, the light-absorbing and light-scattering properties of the film act together to produce its opacity. If the film is low in both light-absorption and light-scattering ability, much of the light reaches the substrate. Such a film therefore hides poorly and is characterized as being low in opacity.

e. Standard Test Substrates

An opacity test substrate generally has an ordered pattern of contrasting colors or shades, usually black and white, although black and grey and grey and white are also used. Juxtaposition of contrasting areas permits both visual observation and photometric measurement of film opacity. For photometric measurements only, individual black glass and white glass panels are sometimes employed to take advantage of their excellent planarity. Clear plastic can also be used as an opacity test substrate by placing it over black-and-white backgrounds. Standard black-and-white opacity test substrates are defined in paint technology as having CIE-Y reflectances of 0.01 (1%) maximum and 0.80 (80%), respectively.[2] White test areas are seldom exactly 80%, but equations are available for correction of photometric values to that standard (see Eqs 1 and 2).

f. Contrast Ratio

The extent to which a paint film obscures or hides the contrasting features of the test substrate on which it is uniformly applied is the measure of its opacity. This is expressed photometrically as the ratio of the luminous (CIE-Y) reflectance over the darker to that over the lighter area of the substrate, which is referred to as the contrast ratio (CR). The Y-reflectance is employed because this CIE parameter is designed to match the sensitivity of the human eye. The CR and the reflectance are expressed as a percentage or as a decimal fraction, the latter to be assumed unless otherwise indicated. A CR value of unity indicates that too little light has reached the substrate for the substrate reflectance characteristics to have a measurable effect on the emergent light flux; thus, there is complete absence of contrast, or complete hiding. Lesser CR values define intermediate levels of contrast, or incomplete hiding. The contrast ratio of a given paint film varies with substrate reflectances and therefore has significance only with respect to a known substrate and primarily to a standard black-and-white substrate as defined in 1.e. In practice, the white area of a commercially available black-and-white substrate normally deviates somewhat from the ideal reflectance of 80%, whereas the black area is normally 1% or less, which has no measurable effect on test results and is therefore treated mathematically as having zero reflec-

[1]The Leneta Company, 15 Whitney Road, Mahwah, NJ 07430.

[2]CIE = Commission Internationale d'Eclairage. Reflectances are measured with specular (mirror) reflection excluded.

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tance. Conventional symbols used in this connection are as follows:

W = the reflectance of the white area of the test substrate,
R_w = the reflectance of the paint film over a white area of reflectance W,
R_0 = the reflectance of the paint film over the black area,
C_w = R_0/R_w, the CR of the applied paint film,
$C_{0.80}$ = $R_0/R_{0.80}$, the CR when $W = 0.80$, and
C = $C_{0.80}$, the abbreviation sometimes used in equations.

In careful hiding power measurements, if the white substrate reflectance deviates more than 0.01 from the standard value of 0.80, one of the following correction equations[3] is employed

$$C_{0.80} = f(R_0, R_w, W) = \frac{WR_0(1 - 0.80R_0)}{R_0(W - 0.80) + 0.80R_w(1 - WR_0)} \quad (1)$$

$$C_{0.80} = f(C_w, R_0, W) = \frac{WC_w(1 - 0.80R_0)}{C_w(W - 0.80) + 0.80(1 - WR_0)} \quad (2)$$

g. Visual Observations of Contrast

Although intermediate levels of contrast cannot be directly quantified by visual means, the eye is qualitatively very sensitive to contrast variations. It can identify equalities or nearly complete absence of contrast with considerable precision, which is the basis for the original as well as several current hiding power methods to be described. Indeed, such visual observations are the basic criteria of what constitutes hiding and hiding power, to which all instrumental hiding measurements trace their validity.

h. Film Thickness

This is usually expressed in thousandths of an inch (mils) or in micrometers (μm). A liquid paint usually contains a substantial quantity of volatiles, so that its dry film thickness (DFT) is substantially less than the original wet film thickness (WFT). The WFT of architectural paints applied in the field are typically in the neighborhood of 3 to 4 mils (75 to 100 μm). With other coating types, it might be as low as 1 mil (25 μm) or as high as 60 mils (1500 μm). With volatile-free liquid coatings, the WFT and DFT are the same except for a possible small increase in density during curing. With powder coatings, for which film formation and curing are concurrent, the term WFT is inapplicable and DFT redundant, so that it is appropriate to refer simply to *film thickness.*

i. Spreading Rate

When paint is applied, whether for test purposes or in actual usage, the area covered per unit quantity of paint is called the spreading rate (SR) for that particular application. When the quantity of coating is expressed volumetrically, as is usual with liquid paints, the SR is usually expressed in square feet per gallon (ft^2/gal) or square metres per litre (m^2/L). When the quantity is expressed gravimetrically, the SR is usually expressed in square feet per pound (ft^2/lb) or square metres per kilogram (m^2/kg). SR is inversely related to the film thickness; thus, for a given paint, the lower the SR, the higher the film thickness and film opacity.

j. Spreading Rate and Film Thickness Relationships

Let

H = spreading rate of the coating (equivalent to SR),[4]
T = wet film thickness (equivalent to WFT),[4]
D = coating density (prior to loss of volatiles),
t = dry film thickness (exclusive of air)[5] (equivalent to DFT),
d = dry film density (displacement density),[5]
N = nonvolatile fraction by weight (equivalent to NVW), and
N_v = nonvolatile fraction by volume (equivalent to NVV).

(1) U.S. Units

$$H\,(\text{ft}^2/\text{gal}) \times T\,(\text{mil}) = 1604.2 \quad (3)$$

$$H\,(\text{ft}^2/\text{gal}) \times t\,(\text{mil}) = 1604.2\,ND \div d \quad (4)$$

$$H\,(\text{ft}^2/\text{lb}) \times T\,(\text{mil}) = 1604.2 \div D\,(\text{lb/gal}) \quad (5)$$

$$H\,(\text{ft}^2/\text{lb}) \times t\,(\text{mil}) = 1604.2\,N \div d\,(\text{lb/gal}) \quad (6)$$

(2) Metric Units[6]

$$H\,(\text{m}^2/\text{L}) \times T\,(\mu\text{m}) = 1000 \quad (7)$$

$$H\,(\text{m}^2/\text{L}) \times t\,(\mu\text{m}) = 1000\,ND \div d \quad (8)$$

$$H\,(\text{m}^2/\text{kg}) \times T\,(\mu\text{m}) = 1000 \div D\,(\text{kg/L}) \quad (9)$$

$$H\,(\text{m}^2/\text{kg}) \times t\,(\mu\text{m}) = 1000\,N \div d\,(\text{kg/L}) \quad (10)$$

(3) U.S.—Metric Unit Conversions

$$H\,(\text{ft}^2/\text{gal}) = H\,(\text{m}^2/\text{L}) \times 40.746 \quad (11)$$

$$H\,(\text{ft}^2/\text{lb}) = H\,(\text{m}^2/\text{kg}) \times 4.8882 \quad (12)$$

$$T\,(\text{mil}) = T\,(\mu\text{m}) \div 25.4 \quad (13)$$

$$D\,(\text{lb/gal}) = D\,(\text{kg/L}) \times 8.3454 \quad (14)$$

(4) Dry Versus Wet Film Relationships[7]

$$ND = N_v d \quad (15)$$

$$t = N_v T \quad (16)$$

$$T = td \div ND \quad (17)$$

2. DEFINITION OF HIDING POWER (HP)

Qualitatively, hiding power is the property of a paint that is manifested as opacity in its films. Quantitatively, it is the

[3]Derived from Eq 39 by equating to $W = 0.80$.

[4]Note that WFT and SR, when the latter is expressed by volume, are inverse ways of stating the same information.

[5]Refers to films containing no air or hypothetically compressed to exclude air.

[6]The following metric notations are identities: kg/L = g/mL = g/cm^3 = g/cc.

[7]These are applicable to both common and metric units since the units all cancel.

spreading rate at which the film opacity is just sufficient to give complete hiding over the specified standard black-and-white substrate (see 1.e). The "complete hiding" point is determined visually in some test procedures and photometrically in others.

a. Visual Hiding Power End-Point

In the visual determination of hiding power, the operator increases the film thickness gradually and records the amount of paint applied at the supposedly exact point of complete hiding. In practice, instead of perceiving such a point, a range of uncertainty is reached beyond which, when hiding seems unquestionably complete, it also seems that the true end-point has been exceeded. To resolve this dilemma and to obtain repeatable results, the operator chooses an end-point at which it seems that only a negligible increase in film thickness is required to completely obscure the contrasting features of the substrate. This so-called *complete hiding* end-point is therefore more accurately described as just short of complete hiding.

b. Photometric Hiding Power End-Point

Uncertainty as to the end-point also exists when measuring hiding power photometrically. A curve of film thickness versus contrast ratio approaches CR = 1 asymptotically, so in theory there is no point at which the contrast is completely obscured. Thus in practice the CR end-point for hiding power measurements must be less than unity. A CR value of 0.98 is generally accepted in paint technology as representing the point of photometric *complete hiding* because it is in fact very close to being visually complete, and a higher CR end-point could not be identified with as much precision. The concept of 98% as the contrast ratio for complete hiding was originally based on the Weber-Fechner law, which states that differences of 2% in reflectance (with moderate illumination) are imperceptible to the human eye [*1*]. Actually, this level of contrast, though slight, is definitely visible.

3. THE ROLE OF PIGMENTS IN HIDING POWER

a. Binders and Pigments

A typical paint binder, by itself, forms a transparent and virtually colorless film that neither absorbs nor scatters light to any appreciable degree and therefore makes no contribution to the hiding power of the coating of which it is a part. This task resides entirely in the pigment constituent of the paint. Pigments are fine-particle-size, insoluble, and usually crystalline solids that when dispersed in paint vehicles contribute to the various properties of the mixture, among which are the optical properties of color and hiding power. Pigments that absorb light strongly over the entire visible spectrum are black; those that are optically selective, absorbing strongly in parts of the visible spectrum and poorly in other parts, are colored, viz. blue, red, yellow, etc., corresponding to the spectral region of nonabsorption. Those that absorb poorly over the entire visible spectrum are white.

b. White Pigments

When dispersed in a paint binder, some white pigments scatter light strongly and thereby contribute to hiding, while others scatter very poorly and make little if any contribution. On that basis white pigments are classified as *hiding pigments* or as *extenders*. White hiding pigments in a paint formulation are sometimes called "prime pigments" as distinguished from the nonhiding "extender" types. The latter are also referred to as "inerts" in view of their apparent passivity with regard to both light absorption and scattering. The difference in scattering behavior between hiding and extender pigments is a function of their refractive indices.

c. Refractive Index

Most pigments are crystalline in nature. If a single crystal of white pigment were grown sufficiently large, it would be perceived as shiny and transparent like glass, and objects observed through it would look bent and distorted as when observed through a glass prism. This is due to the change in direction, referred to as refraction, that occurs when light passes between media in which it has different velocities, as illustrated in Fig. 1. The relationship between the angles in this figure is expressed by Snell's law of refraction

$$n = \sin i / \sin r \tag{18}$$

in which i and r are the angles of incidence and refraction, respectively, and n is a constant referred to as the refractive index, which is the ratio of the velocity of light in the incident to that in the refraction medium. If the large pigment crystal postulated previously is pulverized and dispersed in a paint film, each small particle will refract incident light in the same way as described for the large one. Light will also be partially reflected at the surface, and both refractions and reflections will occur within the pigment particle itself. This activity, endlessly repeated with a multitude of pigment particles as illustrated in Fig. 2 (Ref *2*, p. 1), results in the scattering of the original incident light with concomitant film opacity and paint hiding power. The greater the difference between the refractive indices of the pigment and the surrounding medium, the greater the amount of light scattering. Refractive

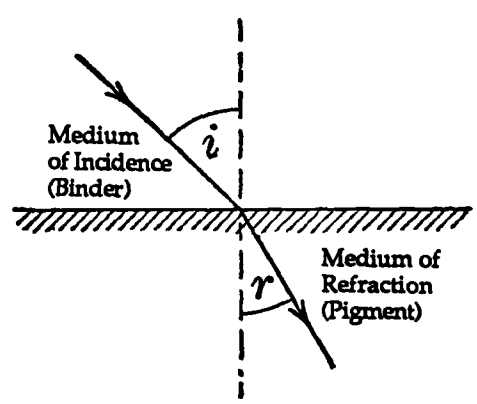

FIG. 1—Bending of a light ray by refraction towards the normal as it enters a medium of lower light velocity (higher refractive index).

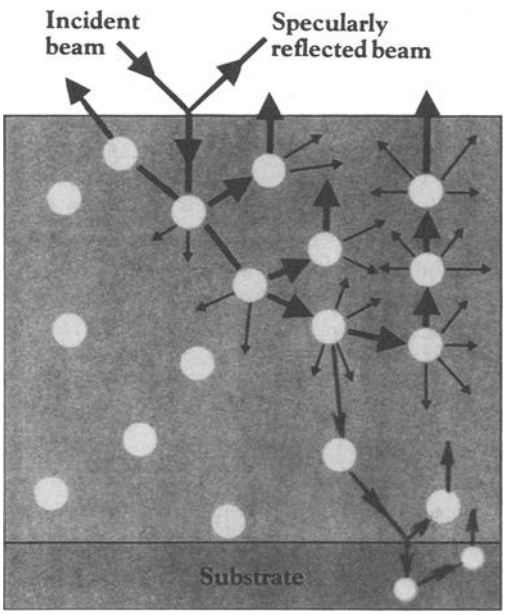

FIG. 2–Light-scattering behavior of a pigmented film.

indices are reported in Tables 1 and 2 with respect to a vacuum as the medium of incidence. Values with respect to air are practically the same. Since white pigments are crystalline in nature, they usually possess different refractive indices along the different crystal axes. Their indices also vary somewhat with the wavelength of the light, generally being higher at the blue (short wave length) end of the spectrum than at the red (long wavelength) end. Tables 1 and 2 give average values [*1*,*3*].

TABLE 1—Refractive index and relative hiding power of some white hiding pigments.

Pigment	Refractive Index	Relative HP, F%[a]
Titanium dioxide (rutile)	2.76	8.8
Titanium dioxide (anatase)	2.55	6.7
Zirconium oxide	2.40	5.3
Zinc sulfide	2.37	5.0
Antimony oxide	2.19	3.5
Zinc oxide	2.02	2.2
White lead carbonate	2.01	2.1
White lead sulfate	1.93	1.6
Lithopone	1.84	1.0

[a]Calculated from Eq 20.

TABLE 2—Refractive index and relative hiding power of some extender pigments.

Pigment	Refractive Index	Relative HP, F%[a]
Barium sulfate	1.64	0.20
Calcium sulfate	1.59	0.08
Calcium carbonate	1.57	0.05
Magnesium silicate	1.57	0.05
Aluminum silicate	1.55	0.03
Silica	1.55	0.03

[a]Calculated from Eq 20.

d. White Hiding Pigments

A rough indication of the relative hiding power of a white pigment can be calculated from its refractive index using the Fresnell equation of reflectivity (Ref *2*, p. 1),

$$F\% = \frac{(n - n_m)^2}{(n + n_m)^2} \times 100 \tag{19}$$

where F is the Fresnell reflectivity, n is the refractive index of the pigment, and n_m is the refractive index of the medium in which it is dispersed. Since the refractive index of a paint binder is in general very close to 1.5, Eq 19 can be rewritten as

$$F\% = \frac{(n - 1.5)^2}{(n + 1.5)^2} \times 100 \tag{20}$$

Tables 1 and 2 illustrate the use of this equation and the general principle that the higher the refractive index of a pigment the greater its hiding power. The relative hiding power values shown therein indicate the magnitude of variation related to index of refraction. Other factors can also affect hiding power substantially, as discussed in Section 9.

e. Extender Pigments

Pigments in this category have low refractive indices in the neighborhood of 1.5. In the form of a powder, with the surrounding medium being air with a refractive index of 1.0, the difference in the two indices produces substantial light scattering, so that extender pigments look white. But dispersed in paint binders, which like themselves typically have a value of about 1.5, they scatter light very poorly and are virtually transparent. This is indicated by the low HP values listed for them in Table 2 as compared with the white hiding pigments in Table 1. Although extender pigments are also referred to as "inerts," the latter term is somewhat of a misnomer. They have an indirect but strong influence on light scattering and hiding power through phenomena referred to as "crowding" and "dry hiding." They also have important effects on other physical properties of paints such as consistency and gloss.

f. Colored Pigments

If a pigment absorbs some wavelengths of light more strongly than others, it reflects back a higher proportion of the weakly absorbed wavelengths and is perceived as having the color of the latter (e.g., red, blue, yellow, etc.). Light absorption of this nature is referred to as "selective." Colored pigments can vary greatly in hiding power depending on their light absorption and light-scattering abilities. With regard to light scattering, as with white pigments this is a function of the refractive index or more specifically the difference in refractive index between the pigment and surrounding medium. Refractive indices of colored pigments vary widely with wavelength, ranging from 1.3 to 2.7. These variations cause such phenomena as bronzing, dichroism, color change with film thickness, and differences in undertone upon dilution with white pigments (Ref *4*, p. 22).

4. EARLY VISUAL HIDING POWER METHODS

a. Brushouts

The earliest methods for determining hiding power employed the practical procedure of brushing the paint uniformly onto combination black-and-white test substrates, increasing the amount of paint in small increments until reaching the point of essentially complete hiding at which the amount of visual contrast was considered negligible. The quantity of paint was determined by weighing the container and brush in grams before and after painting. The corresponding spreading rate (SR) is the hiding power (HP) by definition and was calculated from the equation

$$\text{SR}\,(\text{ft}^2/\text{gal}) = \frac{\text{Test Area}\,(\text{ft}^2) \times \text{Paint Density}\,(\text{lb/gal}) \times 454}{\text{Weight of Paint}\,(\text{g})} \quad (21)$$

For single-pigment paints, the value calculated from Eq 21 can be converted to pigment hiding power using the equation

$$\text{SR}_{\text{pigment}}\,(\text{ft}^2/\text{lb}) = \frac{\text{SR}_{\text{paint}}\,(\text{ft}^2/\text{gal})}{\text{Pigment Concentration}\,(\text{lb/gal})} \quad (22)$$

Variants of these equations provide for the use of metric instead of U.S. units.

b. Early Test Substrates

Originally in the study of hiding power, test surfaces were prepared in individual laboratories by painting black stripes on white-painted panels. In response to the need for standardized test surfaces, studies were made on oil cloth and linoleum having printed checkerboard-type designs [*5*]. The Gardner Contrast Hiding Power Board was a two-square-foot area glass checkerboard with black and white squares painted on the underside of a thin piece of glass (Fig. 3). The first formalized ASTM method used a linoleum checkerboard surface in the brushout test procedure described in 4.a. The Gardner glass board was used in the same way. Since the "complete hiding" end point in those early methods was determined when the paint was freshly applied and still wet, the resultant hiding power value pertained only to the wet hiding power of the paint, not to the dry. This was not a problem in the earliest days of hiding power measurement when typical paints contained relatively little volatile constituent and the opacity of the film therefore did not change markedly while drying. But, with the advent of modern paint formulations containing substantial amounts of volatiles, the composition and with it the opacity of the dry paint film could be substantially different than that of the initially applied film. The need to measure dry hiding power therefore became of paramount importance. As a practical problem in this connection, expensive linoleum and glass test surfaces had to be cleaned for reuse after each test, which made it very difficult to use them for the study of *dry* hiding power. This problem was partly overcome with the introduction of paper test charts circa 1931 that were printed in various designs such as checkerboard, concentric diamond-shaped bands, spirals, crescents, etc., and with various degrees of contrast such as black-white, black-grey, grey-white, and a graded series of stripes from black to white. After printing, a coat of nitrocellulose lacquer or other suitable clear sealer was applied. Many of those chart types became and continue to be commercially available.

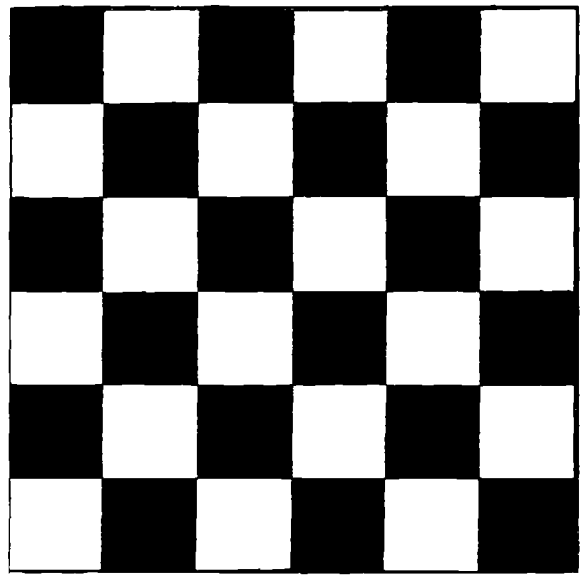

FIG. 3–Gardner contrast hiding power board.

c. Contrast Design and Visual Sensitivity

Kraemer and Schupp [*6*] evaluated contrast surfaces in a variety of designs prepared on glossy photographic paper. These included the customary checkerboard design, a design of narrow 15-mm-wide bands, another with much broader bands, and one with dark half circles on a light background. The results seemed to favor a narrow band design subsequently employed by the Krebs Pigment Co. in preparing the diamond stripe grey and white contrast charts illustrated in Fig. 4. The test area of that chart was 1 ft^2 (0.0929 m^2). The use of a grey-and-white contrast combination was based on the idea that this is more representative than black and white of the degree of contrast encountered by paints in actual use.

d. Relative Dry Hiding Power—Krebs Method

Although the introduction of paper test charts as replacements for linoleum or glass made dry hiding power measurements easier, they were still not easy enough. The problem was that it required the preparation of a considerable number of paint-outs at various spreading rates to obtain one that after drying could be identified with confidence as representing the "complete hiding" end-point. One solution to this problem was to determine comparative or relative dry hiding power. In the Krebs Pigment Co. method, their square-foot grey-and-white diamond stripe chart was used for that purpose in the following manner: A partial hiding ladder of six to eight brushout standards is made by applying a standard paint at spreading rates ranging from 400 to 800 ft^2/gal (10 to 20 m^2/L) and allowing the brushouts to dry. The spreading rates are precontrolled approximately by syringing specified volumes of paint onto each chart and then determined accurately by weight measurements and calculation as described

FIG. 4–Krebs diamond-stripe hiding power chart.

in 4.a. A single test paint panel is likewise prepared at an intermediate spreading rate. After drying, that panel is compared with the standard panels to determine the two that bracket it in contrast. Then by visual interpolation a fairly precise estimate is made of the spreading rate of the standard paint required to match the contrast of the test paint panel. The relative dry hiding power of the test paint is the percent ratio of its spreading rate to that of the standard paint at equal visual contrast, thus

$$\%\,\text{Relative Hiding Power} = \frac{SR_{\text{Test Paint}}}{SR_{\text{Std. Paint}}} \times 100 \qquad (23)$$

e. Pfund Cryptometers

(1) All Black

Introduced in 1919, this was one of the first laboratory instruments made for determining HP [7]. Referring to Fig. 5, A is a plate of black glass whose upper surface is optically flat; B is a transverse groove 10 mm wide and about 2 mm deep. Beginning at the left edge of the groove is a millimetre scale etched in the upper surface of Plate A. C is a plate of clear glass whose lower surface is optically flat. D is a steel shim cemented to C so that a wedge of paint may be formed between the plates. This wedge abruptly becomes "infinitely thick" at B, and so long as hiding is not complete, the line of demarcation is visible. Sliding the wedge to the left eventually

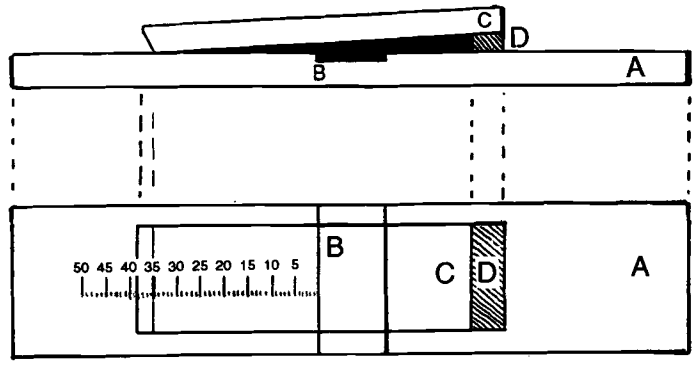

FIG. 5–Diagram of early model of Pfund cryptometer.

causes the line to disappear. The wet film thickness at the point of complete hiding is determined from the scale reading at the toe of the wedge and the thickness of the shim at the heel, from which the HP in ft^2/gal or m^2/L can be calculated using Eq 3 or Eq 7. Dark-colored paints cannot be measured using this instrument because of the lack of contrast with the black glass background. Nelson and Norris of the New Jersey Zinc Co. used this cryptometer to determine HP of colored pigments with results as shown in Table 3. The pastes were prepared by rubbing the colors in No. 0000 lithograph varnish. The rubbing was regulated to represent the maximum development usually obtained in practice. In addition to the regular black glass instrument, they used one specially made with white glass for several measurements.

(2) Black and White

Pfund [8] introduced the black-and-white cryptometer in 1930. It eliminated the well, making cleaning easier, and worked for use with paints of any color because of the black-and-white instead of all-black background. Referring to Fig. 6, the black glass B and the white glass W are fused along line LM. Longitudinal grooves catch the overflow of paint. The wedge is moved to the right to make the line disappear, then to the left to make it reappear. The position of the plate is reversed and the observations repeated. From the mean of all readings, the hiding is calculated as with the all-black cryptometer (4.e.(1)). Comparison of results for white paints shows that the two cryptometer types (all-black and black-and-white) yield the same values within experimental error (Ref 4, p. 22).

(3) Rotary Type

The rotary cryptometer was a short-lived device designed to overcome the jerky movement of the top plate of the regular cryptometer [9]. The wedge of the cryptometers of Figs. 5 and 6 was replaced with a circular glass plate mounted in a metal frame (Fig. 7). The thickness of the film was read on a scale located on the bottom plate. While the movement of the plate was much smoother with this instrument, it was found that bubbles often obscured the end-point.

(4) Assessment of Cryptometers (Ref 4, p. 25)

The cryptometer is a simple instrument requiring only small quantities of paint, and determinations are quickly made. However, reading the end-point is difficult, and the mean of a number of determinations is therefore advisable.

TABLE 3—Hiding power (m^2/kg) of some colored pigments measured with a Pfund cryptometer[a] (Nelson and Norris).

	Black Glass	White Glass
Lampblack	...	105
Carbon Black	...	41
Chromic oxide	29	...
Prussian blue	72	...
Chinese blue	106	...
Blue toner	51	...
Light green	129	...
Medium green	187	...
Deep green	188	...
Light green	101	...
Medium green	167	...
Deep green	181	...
Light green	62	...
Medium green	98	...
Light green	154	...
Medium green	202	...
Deep green	150	...
Green toner	91	...
Green toner dark	130	...
Chrome yellow	23	27
Hansa yellow	31	34
Lt. chrome orange	44	56
Med. chrome orange	17	20
Dk. chrome orange	29	...
Lithol toner	66	...
Lithol toner	75	...
Maroon toner	65	...
Madder lake	36	...
Toluidine toner	137	...
Light para toner	224	...
Deep para toner	160	...
Light para toner	41	...
Deep para toner	35	...

[a]Multiply by 4.9 to obtain HP in ft^2/lb.

Most users can repeat their own results, but agreement among different users is not satisfactory although it is improved by the use of a standard paint [*10*]. Another major disadvantage of cryptometers is that they measure only wet HP. One study [*11*] reported that cryptometers were satisfactory with low-opacity but not high-opacity paints. Consideration of its advantages and disadvantages suggests that the cryptometer is better suited for control work than for specification requirements. The cryptometers shown in Figs. 5 and 6 continue to be commercially available.

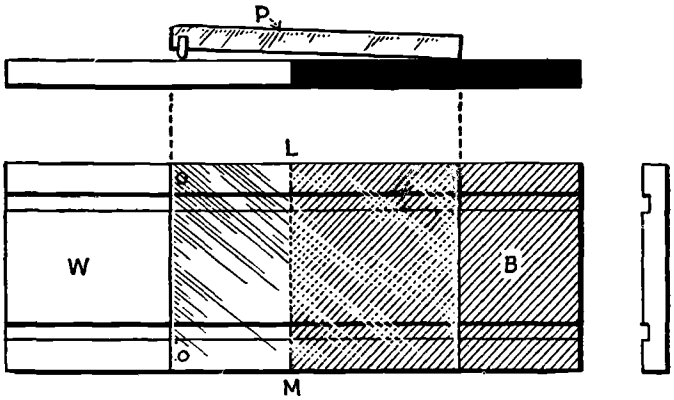

FIG. 6–Pfund black-and-white cryptometer.

f. Hallet Hidimeter

Along with the Pfund cryptometer, the Hallet hidimeter [*12*] was one of the very early devices for evaluating HP. The objective of a regular microscope is replaced by a long tube fitted with a plain ground glass objective; the eyepiece is replaced with a small hole. The principle of the device is the light-diffusing property of ground glass. If a contrast substrate is viewed through a plate of ground glass, the contrast boundaries become more blurred as the distance between plate and substrate increases. If a liquid paint sample is sandwiched between them, it blurs the boundary further, and the distance required to make the boundary disappear decreases. Since that distance is the thickness of the intervening paint film, it is a measure of the hiding power of the paint. This measurement is essentially comparative because it cannot be translated into regular hiding power units.

5. EARLY PHOTOMETRIC HIDING POWER METHODS

a. Pfund Precision Cryptometer

In this device (Fig. 8) a photoelectric cell is used to measure the reflectance of paint contained in a wedge-shaped layer [*13*]. The base plate consists of black-and-white areas B and W, whose boundary is parallel to the length of the plate instead of perpendicular as with the visual cryptometer. The photoelectric device is shifted until a position is found where the reflectance of the paint over the black area is 98% of that over the white area. The film thickness and HP calculations are the same as with the visual cryptometers described in section 4.e.

This cryptometer eliminates the uncertainties of the visual type, as there is no sliding of the top plate over the base plate and no need to estimate visually the appearance and disappearance of an indistinct line. However, it retains the disadvantage of permitting only wet hiding measurements and has therefore been superseded by other photometric devices and methods that permit the measurement of dry hiding power.

b. Hanstock Method

Hanstock [*14*] studied the relationship of light transmission through free paint films to opacity and HP on a black-and-white substrate. For his transmission work, he employed a flicker photometer and found that paint films were perfectly diffusing and that films having the same degree of light transmission had approximately equal opacity. He further showed the correspondence between refractive index, the Fresnel relationship, and HP.

The problem with the transmission concept is that modern paints have so much opacity it is difficult to measure accurately the transmission of films of commercial thickness. Moreover, HP is concerned in practice with paint in intimate contact with opaque surfaces and not as a free film. Consequently, measurement of light transmission through paint films is done today only for very specialized research.

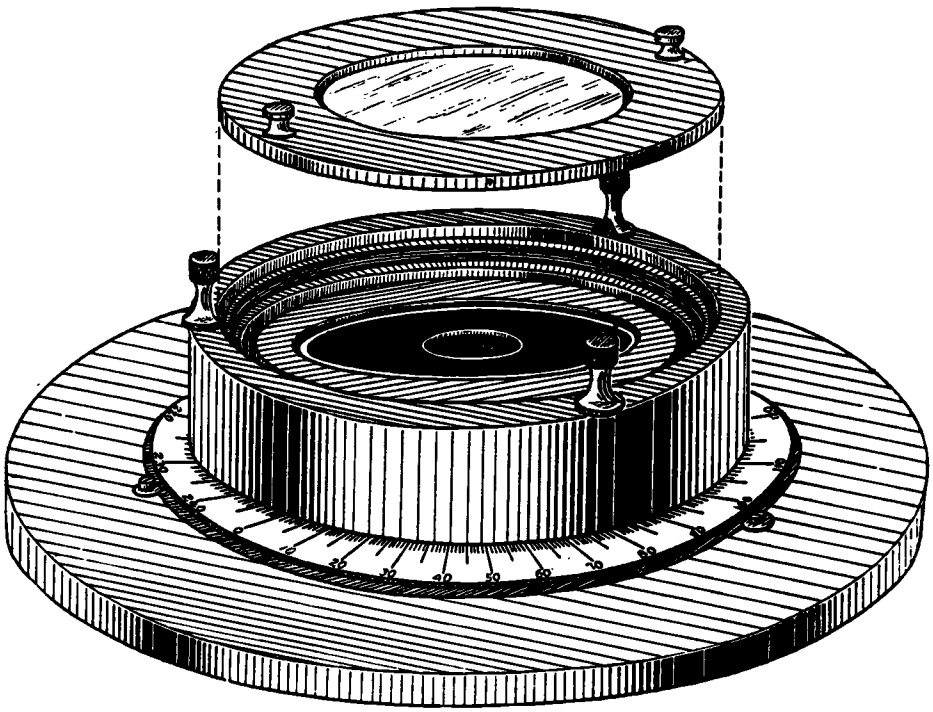

FIG. 7–Rotary cryptometer.

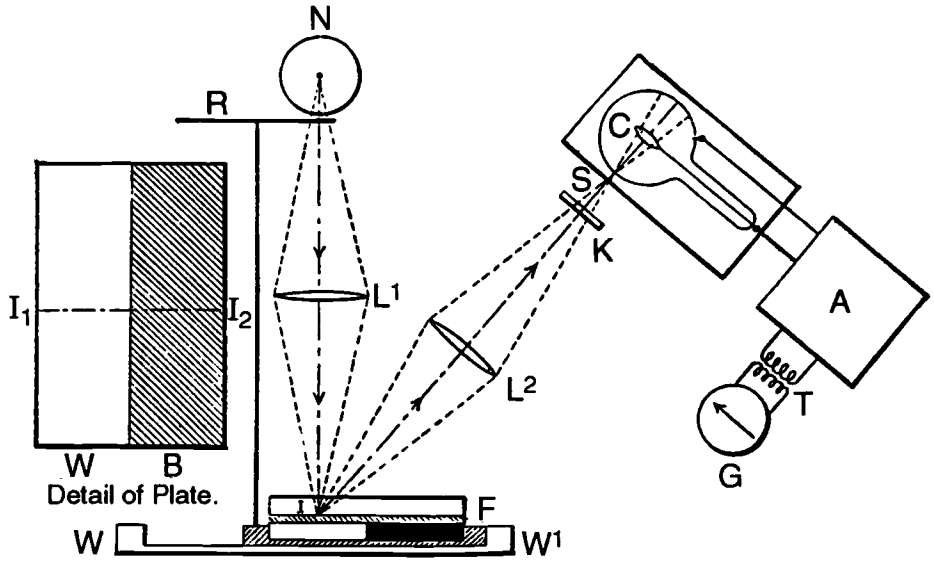

FIG. 8–Pfund precision cryptometer. Uses a photoelectric cell instead of the eye to measure reflectance.

c. Use of the Fell Equation

An empirical relationship between spreading rate (SR) and contrast ratio (CR) was found by Fell and reported by Sawyer [*15*] in the following form

$$\log(\mathrm{CR} \times 10) = m \times \mathrm{SR} + b \qquad (24)$$

where m and b are experimental constants.

Since the graph for this equation is a straight line, it is a simple matter after determining m and b from measurements at two CR levels to find the SR required for any desired CR. This procedure was adapted by Marchese and Zimmerman to determine the hiding power of paints at a contrast ratio of 0.98, and the method was used for many years by the Titanium Pigment Co. (Ref *4*, p. 24). Experience has shown that reasonably satisfactory results can be obtained if the equation is used for interpolation between points close to the desired contrast ratio. But, as pointed out by Switzer [*16*], extrapolation of results can lead to serious errors. He further pointed out that the Fell equation method allows only a single estimate of HP from at least two test applications, thus re-

quiring a considerable effort to obtain an estimate of intralaboratory precision.

d. New York Paint Club (NYPC) Method

This method employed doctor blades to apply films at several thicknesses on black-and-white cardboard hiding power charts. After the films had dried, reflectance, weight, and area measurements were made from which contrast ratios and corresponding wet film thicknesses were calculated. CR values (rather than log 10 CR as in the Fell equation) were plotted against reciprocal film thickness and the HP calculated from the wet film thickness at 0.98 CR. If the white area of the chart deviated appreciably from the standard reflectance of 0.80, the contrast ratio was corrected using Eq 1 or Eq 2. The Club reported that most of the effort in this method was to determine film thicknesses. To minimize that effort they modified the method by casting films on black and white glass plates and determined thicknesses with an Interchemical wet-film thickness gage in accordance with ASTM Test Methods for Measurement of Wet Film Thickness of Organic Coatings (D 1212). Any error in film thickness, of course, carries over to the HP value. According to Mitton, the revised method sacrifices accuracy and precision for speed [*17*]. In addition, graphical averaging makes it burdensome to estimate the precision with which the HP has been determined for the same reason pointed out in 5.c in connection with the Fell equation method.

e. Van Eyken-Anderson Method

The method proposed by Van Eyken and Anderson [*18*] uses CRs and film thicknesses in the same way as the NYPC method described in 5.d, except that films of different thicknesses are applied in a single operation by using a doctor blade having seven clearances. A die is used to prepare uniform area punch-outs of the paper charts to determine spreading rate by the basic weight-area-density-NVW calculation (see Eq 26). The defects of this method are that the small areas used for reflectance and weighing make the achievement of good precision difficult (Ref *4*, p. 31), and there is no provision for correcting CR if the white substrate reflectance differs from 0.80.

f. Federal Test for Dry Opacity

This is Method 4121 of U.S. Federal Test Method Standard No. 141. It is a pass-fail test calling for a minimum dry film contrast ratio at a specified WFT. Black-and-white hiding power charts are used as the test substrate. For routine testing, the paint may be applied either by brush or doctor blade. For referee tests, application is by doctor blade only. The density and the nonvolatile content of the paint are also required. Several drawdowns are made to bracket the specified WFT. The weight of dry paint film is determined for a measured area on each drawdown and the WFT then calculated from the equation

$$\text{WFT (mils)} = \frac{61\,M(\text{g})}{A\,(\text{in.}^2) \times N \times D\,(\text{g/mL})} \tag{25}$$

where

M = the dry film weight,
N = the fractional nonvolatile content of the paint by weight,
A = the film area, and
D = the density of the paint.

The CR of each chart is measured and plotted against the corresponding WFT. From a smooth curve drawn through the points, the CR at the specified WFT is obtained. If this is equal to or greater than the specified CR, then the requirement for dry opacity has been met.

6. GENERAL HIDING POWER METHODOLOGY

a. Film Application

The objective is to determine the spreading rate at a specified level of dry film opacity, which is usually full hiding as perceived visually or corresponding to the contrast ratio: $C = R_0/R_{0.80} = 0.98$. The basic experimental procedure is to apply a uniform film on a suitable test substrate, to observe its opacity either visually or photometrically, and to determine its spreading rate. Since it is not possible to apply a film with precision at a predetermined dry opacity, several such applications need to be made over a range of spreading rates and their results plotted graphically or otherwise interpolated to the desired hiding power end-point. This laborious procedure is exemplified in the visual methods discussed in 4.a and 4.d and in the contrast ratio (CR) methods discussed in 5.e and 5.f. The Fell equation and NYPC methods (5.c and 5.d) attempt to reduce the workload to only two spreading rate determinations by plotting SR against CR or log CR and finding the hiding power end-point graphically on the basis of perceived empirical straight-line relationships. Kubelka-Munk theory (see Section 8) shows how the end-point can be calculated with just one spreading rate determination.

b. Spreading Rate (or Film Thickness) Determination

In both visual and photometric hiding power methods, the procedures for observing film opacity are well-defined and can be performed with dispatch. The experimental task most demanding on the operator's time and ingenuity is to determine the spreading rate or film thickness of the applied coating with good precision. Although gages are available to measure wet and dry film thickness directly and quickly, the most accurate procedure, by far, is to determine the weight of applied paint film on a measured test area and then to calculate the spreading rate or film thickness as described in 4.a and 5.f. The equations in both of those methods contain mixed metric and common units. When the units are all metric, the equations are simpler. Letting M = dry film weight and A = the film area and using the symbolism in 1.j:

$$H\,(\text{m}^2/\text{L}) = \frac{A\,(\text{cm}^2)\cdot N\cdot D\,(\text{kg/L})}{10M\,(\text{g})} \tag{26}$$

$$T(\mu\text{m}) = \frac{10^4 M\,(\text{g})}{A\,(\text{cm}^2)\cdot N\cdot D\,(\text{kg/L})} \tag{27}$$

See 1.j.2 for equations interrelating spreading rate, wet film thickness, and dry film thickness. See 1.j.3 for conversions between metric and U.S. units.

If the volatiles have a relatively low evaporation rate as with most architectural coatings, the film might be weighed rapidly before appreciable loss of volatiles, in which case Eqs 26 and 27 would still apply but with M as the wet film weight and N as unity. The disadvantage of this procedure is that it demands very skillful and speedy manipulation to minimize loss of volatiles before weighing. For that same reason, it is not applicable at all to coatings containing fast evaporating solvents.

With powder coatings, for which the spreading rate is normally expressed on a weight basis, Eq 26 becomes

$$H\,(\mathrm{m^2/kg}) = \frac{A\,(\mathrm{cm^2})\cdot N}{10M\,(\mathrm{g})} \tag{28}$$

Assuming negligible volatile content, the value of N in this equation can be taken as unity.

c. Photometric Measurements

The CIE-Y reflectance is measured because this function defines the human eye's quantitative response to the luminous character of light across the visual spectrum. This is valid for chromatic as well as nonchromatic colors, as reported by Tough [*19*], who found good correlation in a large series of colored paints between visual hiding power measurements and contrast ratio values based on CIE-Y measurements with a spectrophotometer. The end-point of 0.98 CR is effective with colors, although it appears that other end-points, for example CIELAB color difference: $\Delta E = 1.5$, would make some difference in the relative HP of various colored paints [*20*]. However, the simplicity of the 0.98 end-point and its history of validity and general agreement among various workers make it the best choice regardless of color (Ref *4*, p. 31). CIE-Y measurements can be made with the green filter of a tri-stimulus colorimeter or with a spectrophotometer. When properly standardized, results with the two instrument types should be the same. As a precaution, there should be coordination between correspondent laboratories with regard to instrumentation. In all cases, reflectance measurements must be made excluding surface reflection, which is implicit for instruments designed with 0°/45° geometry and optional with most other instrument types.

7. CURRENTLY USED TEST SUBSTRATES

The substrate is generally the major factor affecting the specific experimental details of a test procedure. It is selected or specified on the basis of its adaptability to the type of coating being tested and for its perceived advantages in the required or preferred test procedure.

a. Paperboard Charts

Substrates of this type are described in 4.d. Their employment with baking finishes is limited because of distortion and discoloration at high temperatures, but they are used widely with air-dried coatings for general hiding power observations. Black-and-white charts can be used for precision photometric hiding power measurements by taking appropriate steps to allow for weight variations in the substrate due to humidity and inherent random variations in the area weight of paper. These steps include the use of unpainted control charts and the averaging of multiple test results. Charts with combinations of gray and black, gray and white, and gradations of gray on a white background are used in visual hiding power tests to obtain what are considered to be more practical hiding power measurements.

b. Clear Plastic Film

Polyester is the preferred chemical type. Because of heat distortion, its use is generally confined to air-dried coatings. After the film has dried, a square of convenient size is cut and the area measured. Values of R_0 and R_w are read by placing the painted plastic film alternately on a black and a white background with the underside moistened with a suitable liquid (e.g., mineral spirits or dibutyl phthalate) to remove the air interface and establish good optical contact. The dry film weight is determined as the difference in the weight of the painted and unpainted substrate by stripping off the paint film with a strong solvent.

c. Glass Panels

Individual black and white glass panels are used to take advantage of the superior levelness of glass for casting of uniform films and because the hard, smooth surface permits rapid wet film thickness measurements with an ASTM-type of wet-film thickness gage (5.d). The same information is obtained less rapidly but with much better precision by scraping off and weighing a defined area of dry film and calculating as described in Section 6.b. In some tests, contrast ratios are calculated on the questionable assumption that separate film applications on black and white glass panels are identical in film thickness.

d. Painted Metal Panels

Panels of this type are generally used with coatings that are applied by spraying and cured by baking. The weight of the applied film is determined by weighing the panel before the coating is applied and again after drying. The spreading rate or film thickness is then calculated as described in 6.b. If desired, the dry film thickness can be determined without weighing, though with considerably less precision, by direct measurement with a magnetic or an eddy current thickness gage. Black-and-white panels are used for contrast ratio measurements or for visual observation of opacity. The use of all-black panels is described by Mitton for measuring the hiding power of baking enamels [*21*].

8. KUBELKA-MUNK (K-M) TWO-CONSTANT THEORY

a. Introduction

The light that enters a paint film is subjected to scattering and absorption as described in Section 3, and whatever is not absorbed by the film or substrate eventually reemerges as reflected light. In 1931 Kubelka and Munk [22] published equations defining the optical behavior of a translucent material in terms of two constants referred to as coefficients of scattering and absorption. Steele [23] in 1935 showed how these equations were adaptable to the measuring of paper opacity, and Judd et al. [24] in 1937 did the same in connection with coatings. Kubelka [25] in 1948 rearranged the original equations into new and simplified forms from which Switzer [26] in 1952 developed equations designed specifically for the study of hiding power by expressing the film thickness (or SR) as a function of the CR. Using these equations and their derivatives, the contrast ratio of a coating can be calculated for any spreading rate (or vice versa) from measurements made at only one and its photometric hiding power thereby determined by a single test application. This is in contrast with the more laborious procedure of obtaining CR values at two or more spreading rates for interpolation or extrapolation to the hiding power end-point. The calculations appear formidable but are readily accomplished with a suitably programmed computer. Graphs and tables are also available for this purpose, although not as convenient and accurate as a computer. The experimental steps are straightforward, and, as with most hiding power methods, the most difficult and time-consuming operation is to determine the experimental spreading rate (or film thickness) with sufficient precision. How that is accomplished is the essential difference between various Kubelka-Munk–based methods.

b. Equation Symbols

The symbols used here are based on ASTM Test Method for Hiding Power of Paints by Reflectometry (D 2805-88) as follows:

G = the substrate reflectance
For a white substrate $G = W$.
For a standard white substrate $G = W = 0.80$.
For a black substrate $G = B$.
For a standard black substrate $G = B \leq 1 \approx 0$.

R_G = the reflectance of a film applied over a substrate of reflectance G.

R_∞ = *reflectivity*—a property of the paint—the limiting reflectance of the paint film as it is increased in thickness. Also defined as the reflectance at complete hiding as evidenced by $R_0 = R_w$ over a black-and-white substrate of uniform film thickness.

C_w = the contrast ratio of a film applied at uniform thickness over a black-and-white substrate; thus, $C_w = R_0/R_w$,

$C_{0.80}$ = the contrast ratio over a standard black-and-white substrate, thus $C_{0.80} = R_0/R_{0.80}$.

C = abbreviation for $C_{0.80}$; the two are used interchangeably, thus $C = C_{0.80} = R_0/R_{0.80}$.

T = the film thickness in any stated unit, e.g., μm, mils.

H = the spreading rate in any stated unit, e.g., m²/L, ft²/gal, m²/kg, ft²/lb, cm²/g.

S = the scattering coefficient, a measure of the ability of the paint to scatter light, expressed in units reciprocal to T or the same as H.

K = the absorption coefficient—a measure of the ability of the paint to absorb light, expressed in the same unit(s) as S.

e = 2.718 28 . . . the exponential base for natural logarithms.

P = scattering power—a measure of the ability of a film to scatter light. A unitless film constant defined mathematically by the relationships: $P = ST$ or $P = S/H$.

Subscripts

x indicates an experimentally determined value, e.g., T_x, H_x, P_x.

c indicates a value calculated for a specified contrast ratio C, e.g., P_c, H_c.

0.98 indicates a value calculated for $C = 0.98$, e.g., $H_{0.98}$, $T_{0.98}$.

H indicates a value pertaining to a spreading rate, e.g., C_H, P_H, S_H.

T indicates a value pertaining to a film thickness, e.g., C_T, S_T.

a and b are simplifying functions of R_∞, defined by

$$a = \tfrac{1}{2}(1/R_\infty + R_\infty) \tag{29}$$

$$b = \tfrac{1}{2}(1/R_\infty - R_\infty) \tag{30}$$

From these definitions are derived the additional relationships

$$b = (a^2 - 1)^{1/2} \tag{31}$$

$$R_\infty = a - b = a - (a^2 - 1)^{1/2} \tag{32}$$

Note that R_∞, a, and b are three forms of the same constant, so that the determination of any one of them is equivalent to determining all three. Sometimes they are used together in the same equation.

Additional simplifying functions which can be expressed in exponential-logarithmic form, or using hyperbolic cotangents are

$$U = f(P, R_\infty) = b\left(\frac{e^{2bP} + 1}{e^{2bP} - 1}\right) = b \coth bP \tag{33}$$

and the converse of Eq 33

$$P = f(U, R_\infty) = \frac{1}{2b}\ln\left(\frac{U + b}{U - b}\right) = \frac{1}{b}\coth^{-1}\left(\frac{U}{b}\right) \tag{34}$$

in which

ln = sign of natural logarithms, viz., $\log_e x = \ln x$,

coth = sign of hyperbolic cotangents, defined by $\coth x = \dfrac{e^{2x} + 1,}{e^{2x} - 1}$ and

$\coth^{-1}$ = sign of inverse hyperbolic cotangents, defined by $\coth^{-1} x = \dfrac{1}{2}\ln\left(\dfrac{x + 1}{x - 1}\right)$.

Values of natural logarithms and hyperbolic functions are available in published tables and in calculators. Since the

tangent function is frequently provided without the cotangent, the relationships between the two are stated here as follows

$$\coth x = 1/\tanh x, \coth^{-1} x = \tanh^{-1} 1/x$$

c. Original *K-M* Equations

The original equations are as follows:

For nonopaque films

$$R_G = f(ST, R_\infty, G) = \frac{G/R_\infty - 1 + (1 - GR_\infty)e^{(1/R_\infty - R_\infty)ST}}{G - R_\infty + (1/R_\infty - G)e^{(1/R_\infty - R_\infty)ST}} \quad (35)$$

For opaque films

$$R_\infty = f(K/S) = 1 + K/S - (K^2S^2 + 2K/S)^{1/2} \quad (36)$$

whose converse and more useful form is

$$K/S = f(R_\infty) = (1 - R_\infty)^2/2R_\infty \quad (37)$$

Functional forms are shown in this discussion along with the corresponding explicit forms for a clearer perception of the variables. Sometimes the functional form will be used by itself for both brevity and clarity.

Equation 35 shows the reflectance of a paint film in terms of two basic optical characteristics of the paint: the scattering coefficient, S, and reflectivity, R_∞, and two values that are characteristic of the particular application: the reflectance G of the substrate and the thickness T of the film. Equation 36 shows that R_∞ could be replaced by K in Eq 35, but R_∞ is preferred because the resultant equation forms are much simpler and also because R_∞ can in some cases be measured directly.

d. Scattering Coefficient and Scattering Power

The product ST in Eq 35 is a unitless film constant referred to by Kubelka [*23*] and Judd [*22*] as the scattering power of the film and symbolized here by the letter P. Thus, given that $P = ST$ and employing simplifying forms of R_∞ and the function U of Eq 33, Eq 35 can be rewritten in the much abbreviated form

$$R_G = f(U, R_\infty, G) = f(P, R_\infty, G) = \frac{1 - G(a - U)}{a + U - G} \quad (38)$$

Since film thickness T and spreading rate H are reciprocally interdependent (see Eqs 3 and 7), it follows that $P = S_T T = S_H/H$, with the scattering coefficient (S_T or S_H) being expressed in a unit reciprocal to that of T (e.g., mil^{-1}, μm^{-1}) or in the same spreading rate units as H (e.g., ft^2/gal, m^2/L, ft^2/lb, m^2/kg, cm^2/g). A clarifying concept in which spreading rate units are mandatory is to consider scattering as an entity quantifiable in area units, with the scattering coefficient as the amount of scattering per unit quantity of coating or coating ingredient, and scattering power as the amount of scattering per unit area of film. Spreading rate units have the further advantage over film thickness and reciprocal film thickness of being directly relatable to gravimetric as well as volumetric quantities. Thus, for understandability, convenience, and standardization, it is preferable to use spreading rate units for scattering coefficients and hiding power and more specifically the metric spreading rate units m^2/L and m^2/kg. These are translatable into film thicknesses and U.S. units using the conversion equations in 1.j.3. Equations for the numerical conversion of scattering coefficients expressed in various units to standardized metric spreading rate units are given in Table 4.

e. General K-M Hiding Power Method

The experimental procedure, in brief, is to determine the reflectivity R_∞ of the paint and R_0 and H_x of a nonopaque paint film, from which the scattering coefficient S of the paint is calculated. From R_∞ and S is then calculated the spreading rate H_c at any specified contrast ratio C or vice versa, or more specifically the spreading rate $H_{0.98}$ when $C = 0.98$, which by definition is the hiding power of the paint. The *K-M* equations used in these calculations are derived from Eq 38 (the simplified form of Eq 35) and can be programmed for quick computer solutions.

(1) Determination of Reflectivity R_∞

A paint film is applied uniformly over a black-and-white substrate at normal spreading rate (or film thickness) and dried in the manner usual for the particular coating. After drying, the reflectance values R_0, R_w, and W are measured. If the contrast ratio $C_w = R_0/R_w$ is less than 0.96, the application is repeated as a second coat or at a somewhat higher film thickness. A porous film should not be recoated nor an impractically high film thickness applied in a single coat due to the possible effect on R_∞. If the original or recoated film hides completely, then $R_0 = R_w = R_\infty$. If not, calculate

$$a = f(R_0, R_w, W) = \frac{1}{2}\left(R_w + \frac{R_0 + W - R_w}{WR_0}\right) \quad (39)$$

and from Eq 32:

$$R_\infty = a - (a^2 - 1)^{1/2}$$

The preceding two equations may be programmed sequentially to give

$$R_\infty = f(R_0, R_w, W) \quad (40)$$

(2) Determination of R_0 *and* H_x

This requires the application of a uniform film at a spreading rate (or film thickness) such that the contrast ratio C_w is within the range of 0.96 to 0.985. These limits are established because too low a CR requires excessive extrapolation to the $C = 0.98$ end-point, and higher CR values become increasingly insensitive to spreading rate (or film thickness) variations. If the initial application is outside that range, the application is repeated at a higher or lower film thickness, as required.

TABLE 4—Unit conversion equations for scattering coefficients.

S (m^2/L)	=	S (ft^2/gal) ÷ 40.746
"	=	S (mil^{-1}) × 39.37
"	=	S (μm^{-1}) × 1000
"	=	S (mm^{-1}) × 1
S (m^2/kg)	=	S (ft^2/lb) ÷ 4.888
"	=	S (cm^2/g) ÷ 10
S (m^2/L)	=	S (m^2/kg) × D (kg/L)

The film may be applied on a black-and-white or an all-black substrate. If black-and-white, then the test application can be the same one used for determining R_∞ in 8.e.(1). If an all-black test surface is employed, the indicated contrast ratio range is still required, but since it can't be measured directly, it is calculated from

$$C_{0.80} = f(R_0, R_\infty) = \frac{R_0(1 - 0.80R_0)}{R_0 + 0.80(1 - 2aR_0)} \quad (41)$$

Having obtained a film within the specified contrast ratio range, R_0 is recorded and H_x is determined by a suitable method. Various techniques for determining the spreading rate are available, but the most precise is a weight-area-density-NVW method as discussed in Section 6.b, using applicable Eqs 26 or 27. The dry film weight M in those equations is usually obtained as the difference in the weight of the test area before and after application of the paint. Sometimes, as with black glass, it is obtained by removing a known area of film and weighing it directly. Such weighings can be performed on an analytical balance with great accuracy. The density D and nonvolatile N of the paint must of course also be determined if not already known.

With considerably less precision, the thickness of the dry film can be measured using a caliper or electronic gage on a metal panel, from which the spreading rate can be calculated using one of the following relationships

$$H\,(\mathrm{m^2/L}) = \frac{1000\,ND}{t\,(\mu\mathrm{m})\cdot d} \quad (42)$$

or

$$H\,(\mathrm{m^2/kg}) = \frac{1000\,N}{t\,(\mu\mathrm{m})\cdot d\ (\mathrm{kg/L})} \quad (43)$$

where

N = the nonvolatile fraction by weight (NVW) of the test paint,
D = the density of a liquid paint,
d = the density of the dry (or cured) film, and
t = the thickness of the dry (or cured) film.

(3) Calculation of $H_{0.98}$

Having determined R_∞ of the paint and R_0 and H_x of the test film, $H_{0.98}$ is obtained by the following sequence of calculations:

(a) The scattering power P_x of the test film is calculated from

$$P_x = f(R_0, R_\infty) = \frac{1}{b}\coth^{-1}\left(\frac{1 - aR_0}{bR_0}\right) = \frac{1}{2b}\ln\left(\frac{1 - R_0R_\infty}{1 - R_0/R_\infty}\right) \quad (44)$$

(b) The scattering coefficient S of the paint is calculated from $S = P_xH_x$.

(c) The scattering power P_c of a paint film at the contrast ratio $C = 0.98$ is calculated from

$$U_0 = f(C, R_\infty) = \left[\left(a + \frac{1 - C}{1.60\,C}\right)^2 - \frac{1}{C}\right]^{1/2} + \frac{1 - C}{1.60\,C} \quad (45)$$

and Eq 34

$$P = f(U, R_\infty)$$

which are solved sequentially to give

$$P_c = f(C, R_\infty) \quad (46)$$

(d) The hiding power $H_{0.98}$ is then calculated from $H_c = S/P_c$ where $C = 0.98$.

Calculation steps (a) through (d) can be combined into a single computer program to run as follows

$$\text{INPUT: } R_0, H_x, R_\infty, C\text{—OUTPUT: } S, H_c \quad (47)$$

Note that the same equations and program can be used to calculate the spreading rate H_c for any value of C, not just for $C = 0.98$.

Carrying the calculation sequence back to Eq 40 for a single test application on a black-and-white substrate, the combined program would be

$$\text{INPUT: } R_0, R_w, W, H_x, C\text{—OUTPUT: } R_\infty, S, H_c \quad (48)$$

with the reminder that the contrast ratio $C_w = R_0/R_w$ is required to be in the range 0.96 to 0.985 for these operations to provide reliable information.

(4) Contrast Ratio at a Specified Spreading Rate

Although this is not hiding power as such, it is frequently used as an alternative hiding power criterion. After Step (b) of 8.e.(3), calculate the scattering power P at the specified spreading rate H from: $P_H = S/H$, then calculate the contrast ratio C_H from Eq 33:

$$U_H = f(P_H, R_\infty)$$

and

$$C_H = f(U_H, R_\infty) = \frac{a + U - 0.80}{(a + U)[1 - 0.80(a - U)]} \quad (49)$$

which together give

$$C_H = f(P_H, R_\infty) \quad (50)$$

The computer program for this series of calculations would therefore be

$$\text{INPUT: } R_0, H_x, R_\infty, H\text{—OUTPUT: } S, C_H \quad (51)$$

Going back to Eq 40, for a single test application on a black-and-white substrate the combined program would be

$$\text{INPUT: } R_0, R_w, W, H_x, H\text{—OUTPUT: } R_\infty, S, C_H \quad (52)$$

A basic defect of this and other methods that employ contrast ratio as the criterion of HP is that CR values are only comparative as opposed to spreading rates, which have intrinsic and practical significance.

f. Judd Graph

Prior to the availability of modern computers, *K-M* equations were much too complex for a practicable hiding power test method. Judd [*24*] therefore laboriously worked out a general solution to Eq 35 in the form of a graph reproduced in Fig. 9. The graph relates the four variables R_0, $C_{0.80}$, R_∞, and P so that from any two of them the other two can be determined. It consists of two families of curves for constant values of R_∞ and P, plotted on the coordinates R_0 and $C_{0.80}$.

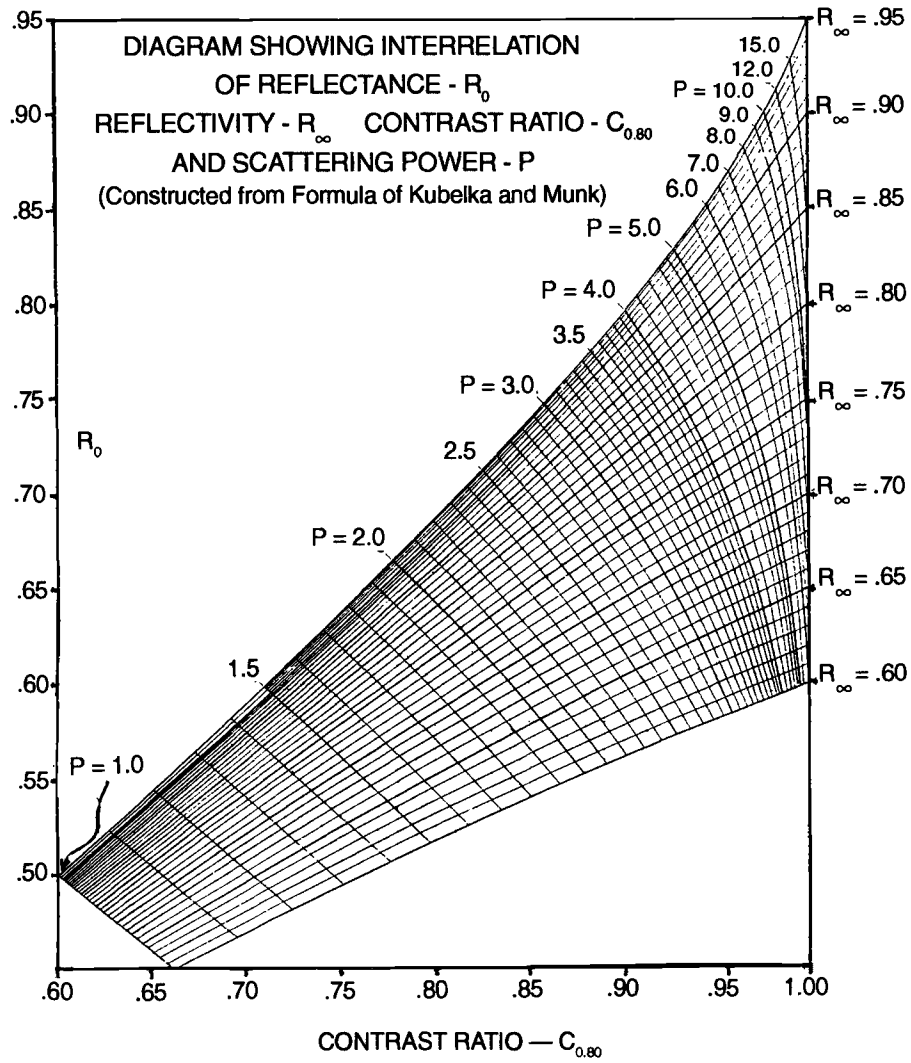

FIG. 9–Judd graph derived from Kubelka-Munk Eq 35.

The P curves were referred to in the original Judd graph as curves of SX (or ST). The portion pertinent to white paints ($R_\infty \geq 0.75$) has been enlarged and is shown in Fig. 10. Experimentally, R_0, R_w, W, and H_x are determined as in 8.e.1 and 8.e.2 for a film applied uniformly on a black-and-white test substrate. If W deviates from 0.80 by more than 0.01, $C_{0.80}$ is calculated using correction Eqs 1 or 2. P_x and R_∞ are determined at the graph point corresponding to $C_{0.80}$ and R_0, and the scattering coefficient of the paint calculated from $S = P_x H_x$. The value of $P_{0.98}$ is located at the intersection of the R_∞ curve with the vertical line for $C = 0.98$. The hiding power is then calculated from $H_{0.98} = S/P_{0.98}$. If desired, the spreading rate can be determined for contrast ratios other than 0.98 in the same way. Conversely, C_H may be determined for any specified value of H by first calculating: $P_H = S/H$, then finding the desired value of C_H at the intersection of the curves for the determined P_H and R_∞.

The Judd graph is also useful for depicting the basic optical properties of paints. It shows that paints with high S values are lighter over black backgrounds than paints of the same reflectivity with low S values. Also, if their S values and film thicknesses are the same, paints with high reflectivity are poorer in hiding than paints of low reflectivity. The latter fact may be demonstrated as follows: Suppose a portion of paint for which $R_\infty = 0.85$ is tinted with a black colorant to an R_∞ value of 0.78 and the untinted and tinted paints are applied at the same thickness such that $P = 5.0$. From Fig. 9, or more accurately from Fig. 10, it can be determined that the colorant addition has increased the contrast ratio to 0.965 from its original value of 0.945, representing a considerable increase in visual film opacity. To determine what this amounts to in terms of photometric hiding power, the P values of the untinted and tinted paints at the intersection of their R_∞ curves with the vertical line $C = 0.98$ are found to be 7.5 and 6.0, respectively. Since S is unaffected by tinting, the spreading rate change at $C = 0.98$ is calculated thus

$$\frac{H_{\text{tinted}}}{H_{\text{untinted}}} = \frac{P_{\text{untinted}}}{P_{\text{tinted}}} = \frac{7.5}{6.0} = 1.25$$

representing an increase of 25% in hiding power by tinting to a lower R_∞ value. This hiding increase was obtained at negligible monetary cost but at a sacrifice in paint quality in regard to brightness of appearance. For that reason, in evaluating a series of paints experimentally, a fair comparison requires that all R_∞ values be adjusted by tinting to that of its lowest reflectivity member. Examination of the Judd graph

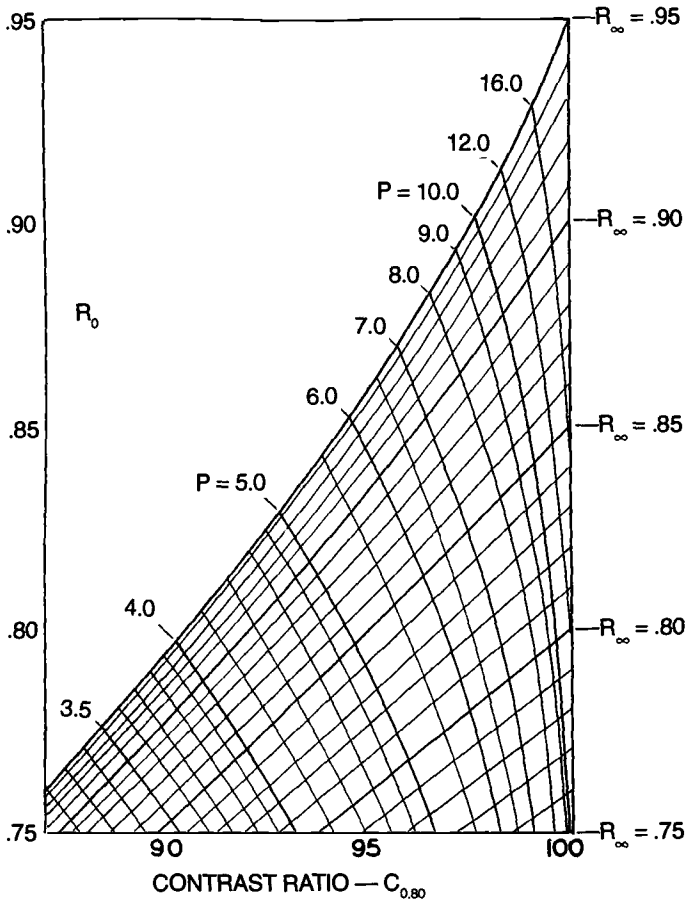

FIG. 10–Judd graph derived from Kubelka-Munk Eq 35—a portion of Fig. 9 enlarged.

shows that, after adjustment to the same R_∞ value, films of the different paints applied at the contrast ratio $C = 0.98$ all have the same $P_{0.98}$ value, and, since $H_{0.98} = S/P_{0.98}$, their hiding powers will be directly proportional to their scattering coefficients. Thus the scattering coefficient alone can be an adequate hiding power comparator, without actually tinting the individual paints.

g. Mitton Graph and Table [27]

As with the Judd graph, these provide precalculated solutions to *K-M* equations, but with much greater precision. They were designed for the experimental procedure described in 8.e, in which R_0 and H_x are determined for a film applied on an all-black test surface, and R_∞ is determined in a separate test application. The test surface of choice is black float glass because the extremely level nature of the surface permits the application of very uniform films with a doctor blade. Mitton also describes the use of all-black metal panels to test spraying/baking-type finishes [*21*]. The graph is derived from Eq 44: $P = f(R_0, R_\infty)$ and is plotted as a family of curves at constant R_∞ on coordinates of scattering power P and reflectance R_0. The ordinate is indicated as "*ST* (Factor *B*)," which is the same as P, and the abscissa as R_B, which is usually and in this case necessarily the same as R_0. It consists of a small-scale index graph (Fig. 11) divided into 31 sections, each then expanded to a much larger scale on a separate sheet. Figure 12 shows one of the expanded sections.

Associated with the Mitton graph is a table of Factor *A* values derived from Eq 46: $P_c = f(C, R_\infty)$, in which Factor $A_c = 1604.2/P_c$. Values of Factor A_c are given in this table for $C = 0.98$, 0.95, and 0.93, for all values of R_∞ from 0.08 to 0.98 (8 to 98%). The C value of most interest for hiding power calculations is 0.98, representing full photometric hiding as defined in Section 2.b. If desired, P_c is easily calculated from Factor A_c.

The graph and table are typically used as follows: After determining R_∞ and R_0 experimentally, the index graph is consulted in order to select the appropriate expanded graph on which the scattering power P_x of the experimental paint film is to be found. Factor $A_{0.98}$ is determined from the table for the measured value of R_∞. At this point either the film thickness T_x or spreading rate H_x of the test film associated with R_0 is determined. If, as Mitton intended, T_x is determined in mils, then the scattering coefficient S is calculated in reciprocal mils from $S = P_x/T_x$, and the hiding power is calculated from the equation

$$H_{0.98}\,(\text{ft}^2/\text{gal}) = S\,(\text{mil}^{-1})\cdot A_{0.98}$$

The preceding simple relationship holds when S is expressed in reciprocal mils and hiding power in ft²/gal. If the spreading rate in m²/L is determined instead of the film thickness, then after determining P_x and R_∞, the scattering coefficient is calculated as: $S\,(\text{m}^2/\text{L}) = P_x \cdot H_x\,(\text{m}^2/\text{L})$ and the hiding power calculated from

$$H_{0.98}\,(\text{m}^2/\text{L}) = \frac{S\,(\text{m}^2/\text{L})\cdot A_{0.98}}{1604.2} = \frac{S\,(\text{m}^2/\text{L})}{P_{0.98}}$$

At a later date Mitton commented that graphical and tabular aids for Kubelka-Munk calculations had become unnecessary with the advent of inexpensive programmable calculators [*28*]. Nevertheless, the Mitton graph and table continue to be used in a number of important test methods, and both the Judd and Mitton graphs are useful for instructional purposes.

h. Typical Kubelka-Munk Hiding Power Results

Tables 5, 6, and 7 are based on the testing of various commercial paints and pigments. They are intended to illustrate magnitudes of hiding power and scattering coefficient values encountered in *K-M* hiding power measurements. The scattering coefficient values are intended to supplement and clarify, by specific examples, the relationships shown in Table 4. With regard to pigments (Table 7), it is of course dispersions that are actually measured and the values for the pigments then calculated from their concentrations in the dispersions. For example

$$\frac{H_{\text{pigment}}\,(\text{m}^2/\text{kg})}{H_{\text{coating}}\,(\text{m}^2/\text{L})} = \frac{S_{\text{pigment}}\,(\text{m}^2/\text{kg})}{S_{\text{coating}}\,(\text{m}^2/\text{L})} = \frac{1}{\text{Pigment Conc. (kg/L)}}$$

The values in Table 7 should be considered as comparative because the hiding power of pigments can vary widely depending on the conditions of measurement (Ref *4*, p. 34), being effected by PVC, effectiveness of dispersion, the presence of other pigments in the same dispersion, and the nature of the vehicle. Even within a specific chemical class it can vary considerably depending upon the particular method of

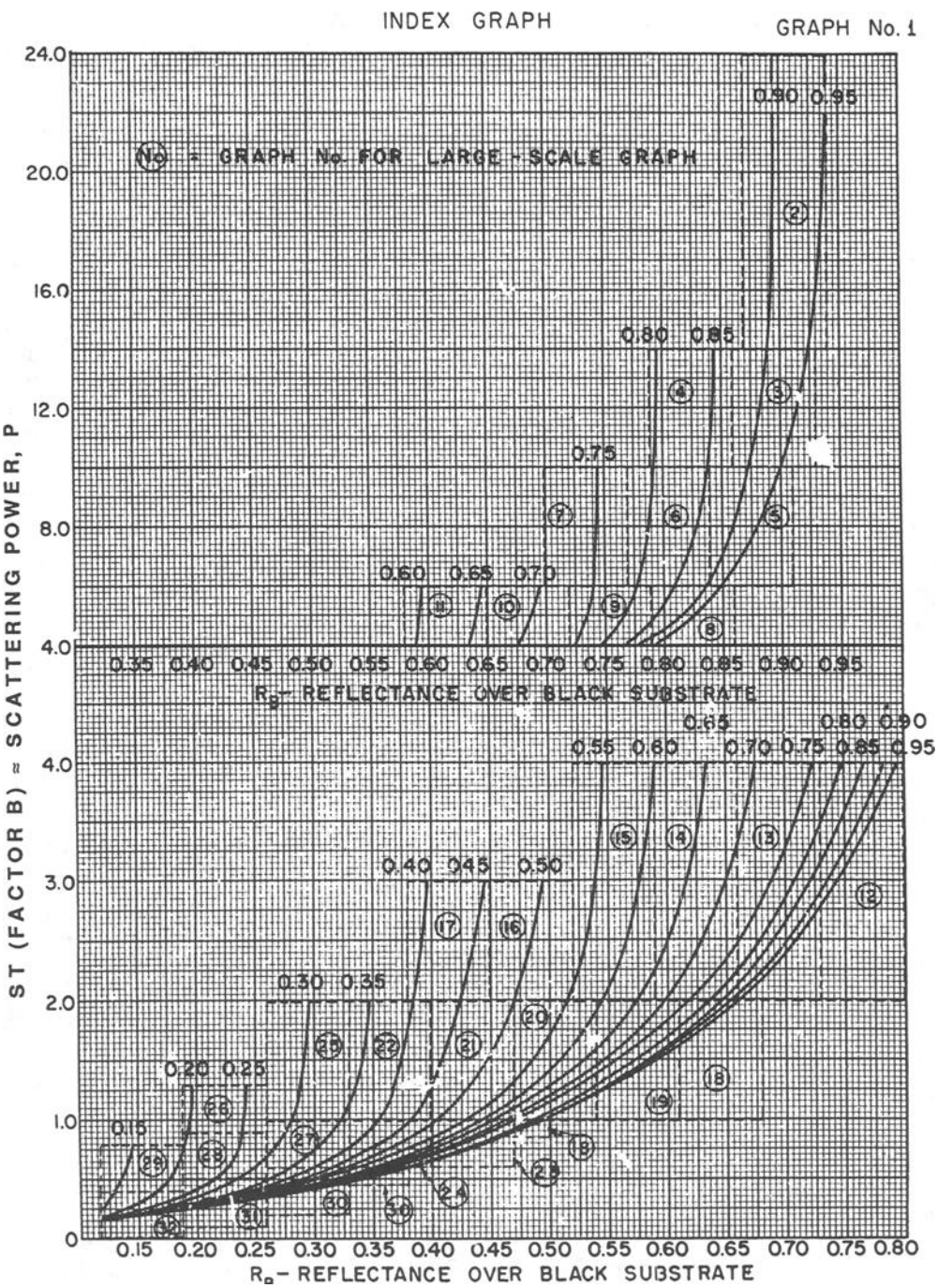

FIG. 11—Mitton graph of Kubelka-Munk Eq 44.

manufacture employed. Nevertheless, it is frequently useful to determine pigment hiding power values for a comparison of their efficiency under specified conditions.

i. Theoretical Problems and Practical Considerations

The validity and usefulness of the Kubelka-Munk equations in hiding power calculations are predicated on the constancy of the scattering coefficient S over a suitably wide film thickness range. Judd [*24*] studied this question in connection with water-borne paints and vitreous white enamels and concluded that at practical film thicknesses S is constant within experimental error. The writer in his laboratory obtained essentially constant S values within a wet film thickness range of 100 to 50 μm (10 to 20 m^2/L, 400 to 800 ft^2/gal) for white alkyd gloss, latex gloss, and latex flat paints. Moreover, the effect of any variation of S with film thickness that might occur is minimized in experimental practice by casting films with contrast ratios fairly close to the 0.98 CR hiding endpoint, as called for in 8.e.(2). This is not difficult to do.

Refractive indices and resultant scattering coefficients vary with the wavelength of light. Thus the effective scattering coefficient of a paint is actually an average for all of the

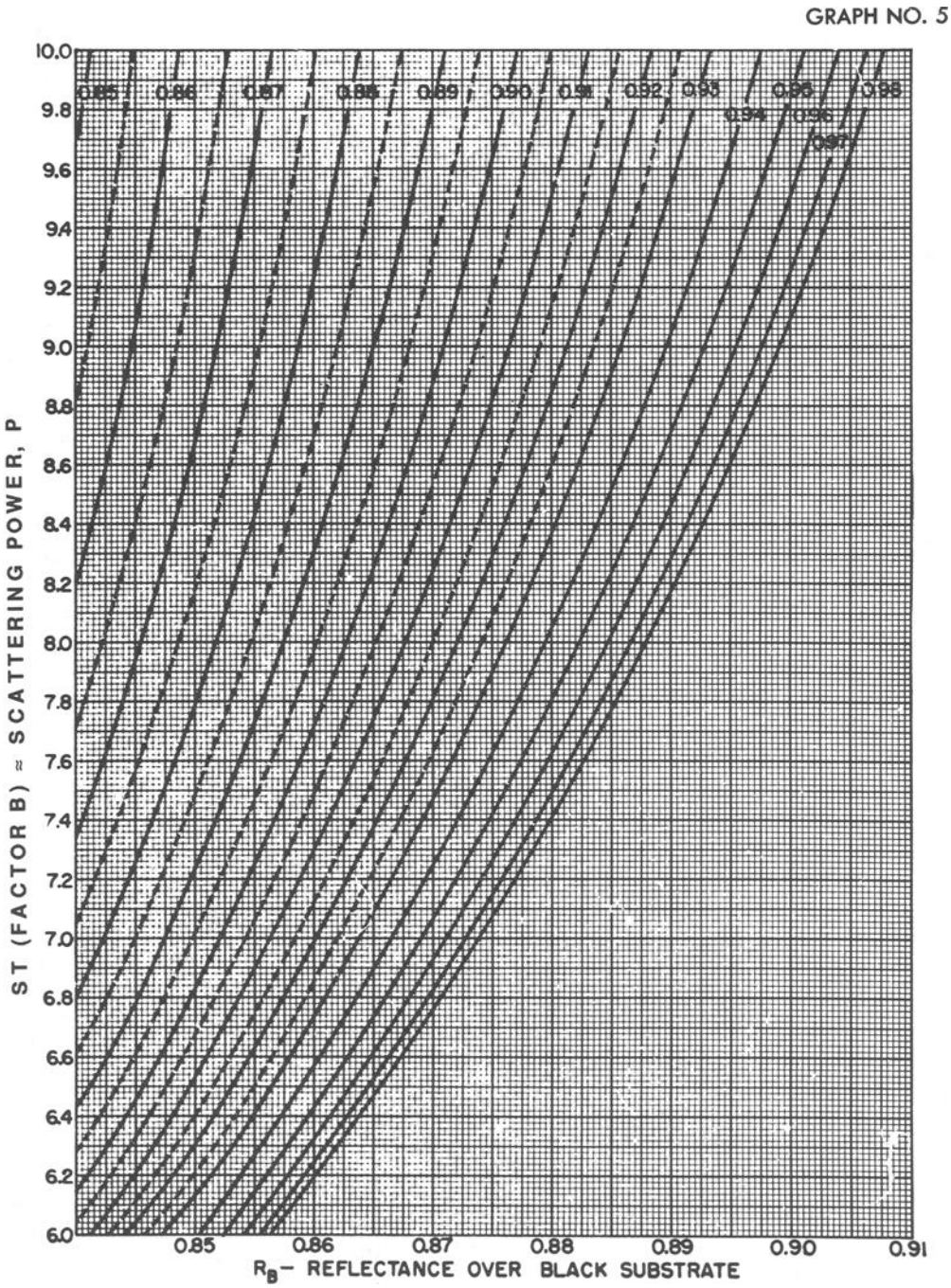

FIG. 12–Mitton graph—expansion of Sector 5 in Fig. 11.

encountered wavelengths. With nonchromatic paint films, the wavelength composition of the light flux remains constant and therefore so does the scattering coefficient upon which constancy the validity of *K-M* equations is predicated. Chromatic paint films, however, absorb light selectively and therefore change the composition of broad-band illuminants with a resultant change in the effective scattering coefficient. This would in theory appear to disqualify chromatic paints from Kubelka-Munk hiding power calculations. In practice, however, the equations are used successfully for that purpose (Ref *29*; Ref *4*, p. 31), which is undoubtedly related to the previously noted fact that the experimental measurements are made fairly close to the hiding power end-point (C = 0.98), so that the Kubelka-Munk extrapolation and thus any associated error is relatively small.

As discussed by Mitton (Ref *4*, p. 27), Kubelka-Munk theory has been questioned because it is "phenomenological" rather than based on fundamental theoretical considerations, and the measurements and equations omit needed corrections for surface reflection that are theoretically substantial. However, in experimental practice the errors are generally small despite the theoretical defects. Simpson took note of this in his comment that when uncorrected values of S and K are inserted back into the uncorrected *K-M* equations, "it would

TABLE 5—Air-dried architectural alkyd coatings—hiding power and scattering coefficient data (Ref *29*; Ref *4*, p. 33).

	Gloss White	Semi-Gloss White	Flat White	Gloss Gray	Gloss Orange	Gloss Yellow	Gloss Green
R_∞ average	0.8798	0.8679	0.9119	0.5654	0.3910	0.6682	0.6940
$P_{0.98}$ (unitless)	8.510	8.158	9.436	3.394	2.150	4.436	4.759
Metric Units							
$H_{0.98}$ (m^2/L)	7.706	8.330	10.32	19.71	15.48	8.629	13.57
$T_{0.98}$ (μm)	129.8	120.0	96.92	50.74	64.60	115.9	73.7
S (m^2/L)	65.58	67.95	98.39	66.89	33.28	38.28	64.58
S (μm^{-1})	0.0656	0.0680	0.0984	0.0669	0.0333	0.0383	0.0646
U.S. Units							
$H_{0.98}$ (ft^2/gal)	314.0	339.4	420.4	803.0	630.8	351.6	552.8
$T_{0.98}$ (mils)	5.109	4.726	3.816	1.998	2.543	4.562	2.902
S (ft^2/gal)	2672	2769	4009	2725	1356	1560	2631
S (mil^{-1})	1.665	1.726	2.499	1.699	0.8455	0.9723	1.640

NOTE: Values are shown here to four significant figures for illustrative purposes only. Experimental precision is in no case to more than three significant figures.

TABLE 6—Powder coatings—Representative hiding power and scattering coefficient data.

	White	Light Gray	Orange
R_∞	0.8234	0.6860	0.4389
$P_{0.98}$ (unitless)	7.011	4.655	2.449
Metric Units			
$H_{0.98}$ (m^2/kg)	18.09	20.22	10.26
Density (kg/L)	1.60	1.66	1.41
$T_{0.98}$ (μm)	34.55	29.79	69.12
S (m^2/kg)	126.8	94.13	25.13
U.S. Units			
$H_{0.98}$ (ft^2/lb)	88.3	98.7	50.1
Density (lb/gal)	13.35	13.85	11.77
$T_{0.98}$ (mils)	1.36	1.17	2.72
S (ft^2/lb)	619.2	459.5	122.7

NOTE: Derived from test results obtained by ASTM Subcommittee D01.51 on Powder Coatings.

TABLE 7—White pigments—hiding power and scattering coefficient values[a].

	Lead Carbonate	Zinc Oxide	Zinc Sulfide	Anatase TiO_2	Rutile TiO_2
R_∞ (estimated)	0.91	...	...	...	...
$P_{0.98}$ (unitless)	9.5	...	...	...	...
Metric Units					
$H_{0.98}$ (m^2/kg)	3.1	4.1	11.9	23.5	30
S (m^2/kg)	29	39	113	223	285
U.S. Units					
$H_{0.98}$ (ft^2/lb)	15	20	58	115	147
S (ft^2/lb)	140	190	550	1090	1390

[a]Based on reported hiding power values at a PVC of 28% [*30,31*].

appear that an approximately correct answer is obtained" (Ref *2*, p. 111).

j. Calculation of Hiding Power from Tinting Data

Initially the S and R_∞ values of a standard white paint are determined in accordance with the procedure described in 8.e. The K value of the paint can then be calculated from Eq 37: $K/S = (1 - R_\infty)^2/2R_\infty$.

From 8.d, S and K can be considered as concentrations of "scattering" and "absorption" per unit weight or volume. The K value of a black tinter is determined by adding a measured ratio to the standard paint sufficient to reduce the reflectivity to about 0.40. The K value of the tinted paint is its initial K value plus the tinter contribution, thus

$$K_2 = K_1 + XK_t \quad \text{(a)}$$

from which

$$XK_t = K_2 - K_1 \quad \text{(b)}$$

and dividing through (b) by the common value of S

$$XK_t/S = K_2/S - K_1/S \quad \text{(c)}$$

in which

K_t = the absorption coefficient of the tinter,
X = the ratio of tinter to paint,
K_1 = the initial K value of the paint,
K_2 = the K value of the paint after tinting, and
S = the scattering coefficient of the paint.

The ratios K_2/S and K_1/S are calculated from measured values of R_∞ for the tinted and untinted paints using Eq 37: $K/S = (1 - R_\infty)^2/2R_\infty$. If the standard paint is an untinted white with a reflectivity no lower than 0.93, then its absorption contribution K_1 is considered negligible compared with that of the tinter, in which case K_1/S is dropped from Eq (c) to give

$$XK_t/S = K_2/S \quad \text{(d)}$$

The absorption coefficient K_t of the tinter can be calculated from Eqs (c) or (d) since all other terms in these equations are known.

Having determined K_t, the S-value of a test paint can be determined using the same tinting procedure and equations as before, but this time calculating unknown S from known K_t instead of vice versa. With the values S and R_∞ of the test paint having thus been determined, its hiding power $H_{0.98}$ can be calculated as in 8.e.(3)(c) and (d) without the tedious requirement of measuring the spreading rate.

Experimental evidence for the validity of this procedure is given by Mitton and Jacobsen [*32*], who, equating the tinting

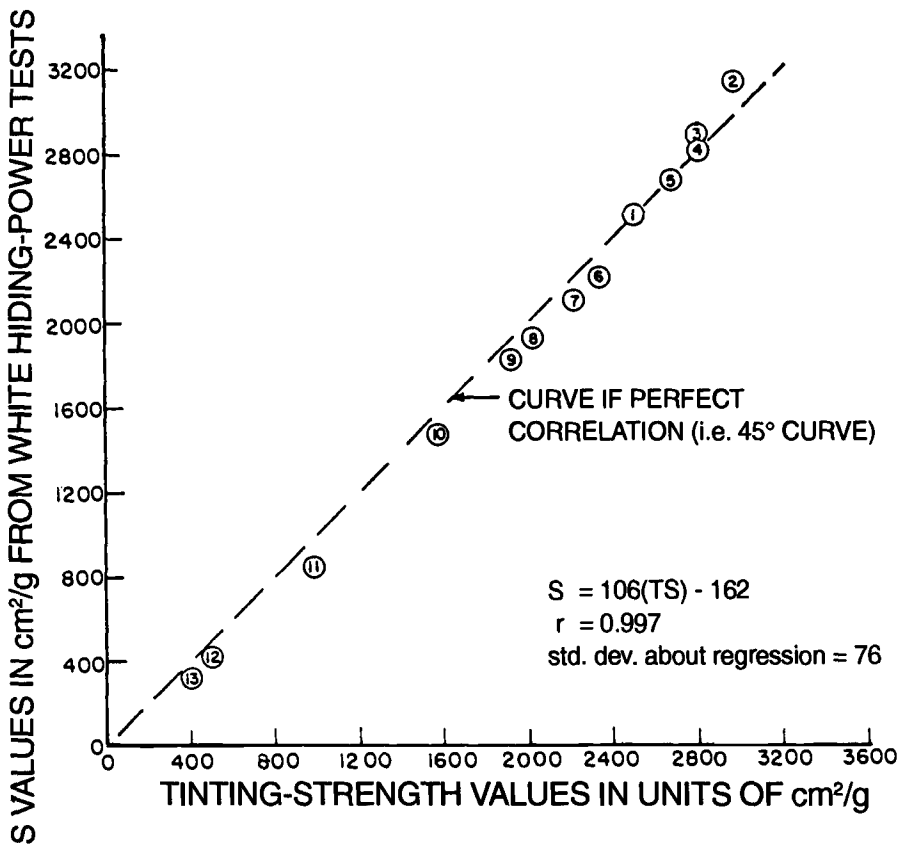

FIG. 13—Scattering coefficients determined by tinting and by hiding power tests.

strength of a white pigment with its scattering coefficient, measured S (cm²/g) for a number of white pigments by direct hiding power measurement and by the tinting procedure. As shown in Fig. 13, the correlation between the two methods is very close. If this simplified method is to work, the K value of the black tinter must be the same in any paint being tested. Also, the tinter must not change the degree of dispersion of the white pigment so as to cause a change in its S value. These conditions are not always met, so that it is safest to apply the method only under favorable circumstances, when interaction of tinter and paint are known to be negligible.

k. Determination of Relative Hiding Power of Untinted White Paints from Tinting Data

For this purpose there is no need to determine the K value of the tinter as in 8.j. An equal ratio of black tinter is added to Comparison Paints A and B, sufficient to reduce their R_∞ values to about 0.40. The R_∞ values of Paints A and B are measured before and after tinting and the four corresponding K/S values calculated from Eq 30. Then, as in Eq (c) of 8.j, for Paint A:

$$XK_t/S_A = K_{A2}/S_A - K_{A1}/S_A \qquad \text{(a)}$$

for Paint B:

$$XK_t/S_B = K_{B2}/S_B - K_{B1}/S_B \qquad \text{(b)}$$

Next, dividing Eq (b) into Eq (a), X and K_t cancel to give

$$S_B/S_A = (K_{A2}/S_A - K_{A1}/S_A) \div (K_{B2}/S_B - K_{B1}/S_B) \qquad \text{(c)}$$

If the comparison paints are both untinted high reflectance whites then, as pointed out in 8.j, the untinted K-values can be considered negligible and Eq (c) becomes

$$S_B/S_A = K_{A2}/S_A \div K_{B2}/S_B \qquad \text{(d)}$$

As stated at the end of 8.f, at the same reflectivity R_∞, the HP values of Paints A and B will be in the same ratio as their scattering coefficients.

9. FACTORS AFFECTING WHITE HIDING POWER

As shown in Tables 1 and 7, rutile titanium dioxide is by far the most effective of the white hiding pigments in producing light scattering and hiding power, which is true on a cost as well as a weight basis. This fact has effectively eliminated the use of other white hiding pigments except for special properties or considerations. The important variables that determine the scattering and hiding efficiency of a titanium dioxide pigment in a paint are: (1) its mean crystal and particle size, (2) the state of pigment dispersion, (3) its concentration in the paint film, and (4) film porosity.

a. Crystal and Particle Size

By decreasing the particle size of the pigment, the number of particles and surfaces for light reflection and refraction increase, and the light scattering ability of a given quantity of pigment will therefore tend to be enhanced. However, if the particle size is too small in relation to the wavelength of light, the wave front passes around rather than through it, so there is no light scattering, and the dispersion is transparent. Obviously, there is some intermediate optimum size related to the wavelength of light at which maximum scattering efficiency is obtained. The wavelength of the visible spectrum ranges from approximately 0.4 to 0.7 μm, peaking in luminosity at 0.55 μm. The mean crystal size for maximum opacity ranges from approximately 0.20 to 0.30 μm depending on both the PVC and the fraction of the pigment consisting of single crystals. Commercial grades of titanium dioxide developed for high-gloss finishes exhibit a single-crystal content of about 20% and have a mean crystal size between 0.22 and 0.24 μm. The adverse effect of lesser crystal size in such formulations is shown in Table 8 [*33*].

b. Pigment Dispersion

The process of obtaining a satisfactory dispersion involves the wetting of the pigment by the dispersion medium to displace air, breakdown of larger particles by milling, and stabilization after the dispersion has been obtained. With alkyd media, standard grades of titanium dioxide disperse easily and develop full hiding with very little milling. Thus, the main reason for milling alkyd dispersions is to reduce or eliminate oversize particles that effect the appearance of the film. With latex paints, milling can have an important effect on opacity depending on the grade of pigment employed [*33*], but the appearance factor is also an important consideration, particularly with semigloss and gloss finishes.

A major factor affecting the efficiency of TiO_2 in the completed formulation is the phenomenon referred to as "flocculation," which is the formation of large particle groups or "floccules" due to weak forces of cohesion. Floccules are easily broken down but can spontaneously and quickly recur in the wet paint or drying paint film. Despite their weak bonding, floccules have the optical effect of increasing the mean particle size, thereby decreasing the scattering efficiency of the pigment. An auxiliary phenomenon related to increased particle size is the preferential scattering of longer wavelengths. Balfour and Hird took advantage of this phenomenon to quantify pigment flocculation by measuring back-scattered infrared radiation (wavelength 25 μm) from a dried paint film to obtain what they refer to as a "flocculation gradient" [*34,35*].

TABLE 8—Scattering coefficient of a 20% PVC TiO_2-alkyd paint film versus crystal size of pigment.

S, μm^{-1}	Mean Crystal Size, μm
0.76	0.24
0.73	0.20
0.64	0.16

c. Pigment Concentration

In Section 3.c it was pointed out that a very large single crystal of a white hiding pigment is actually transparent. Without undertaking a theoretical analysis, it is to be expected that as the concentration of pigment increases and its particles become more crowded, they approach the optical condition of a very large particle with resultant loss of scattering efficiency and hiding power. The "crowding" effect was studied by Stieg [*36–38*], whose results were used by Mitton (Ref *4*, pp. 34–35) to draw curves of hiding power $H_{0.98}$ versus PVC for pure rutile and anatase titanium dioxide in alkyd enamels. These are shown in Fig. 14, in which HP is expressed in ft^2/lb of nonvolatile matter. If the paint is formulated at 50% nonvolatile by volume, the hiding power results would be half that shown in the figure, but the shape of the curves would be unchanged. Note the maximums in the curves at 25 to 30% PVC, above which hiding power actually begins to decrease with increasing concentration of pigment. When calculated in terms of ft^2/lb of pigment, the results appear as shown in Fig. 15, clearly indicating the drastic decrease in TiO_2 efficiency due to crowding.

Stieg [*36*] found empirically that the relationship between TiO_2 hiding power and PVC, as shown in Fig. 15, could be expressed by the equations

$$\text{rutile: } H_{0.98}\,(\text{ft}^2/\text{lb}) = 370\text{-}410\,(\text{PVC})^{1/3} \quad (53)$$

$$\text{anatase: } H_{0.98}\,(\text{ft}^2/\text{lb}) = 290\text{-}330\,(\text{PVC})^{1/3} \quad (54)$$

The PVC values in these equations are decimal fractions. Expressed in metric units, the equations become:

$$\text{rutile: } H_{0.98}\,(\text{m}^2/\text{kg}) = 75.7 - 83.9\,(\text{PVC})^{1/3} \quad (55)$$

$$\text{anatase: } H_{0.98}\,(\text{m}^2/\text{kg}) = 59.3 - 67.5\,(\text{PVC})^{1/3} \quad (56)$$

The question has been studied [*36,39*] of whether extenders added to a gloss or semigloss paint film might tend to increase the spacing of the TiO_2 pigment and thereby its scattering efficiency. The physical picture that emerges is of large particle-size extenders acting as massive intrusions having no effect on the original TiO_2 spacing, and of fine particle-size extenders dispersing uniformly so as to increase TiO_2 spacing, but no differently in this respect than an equal volume of binder. Consequently, when binder is replaced by an equal volume of large particle-size extender, TiO_2 efficiency decreases, whereas with small particle-size extenders, TiO_2 efficiency has been found to remain essentially the same and in no case improved.

d. Film Porosity

The preceding relationships pertain to pigment concentrations at which there is sufficient binder to wet the pigment completely and form a continuous phase, which means below the critical pigment volume concentration (CPVC). Above the CPVC, the dried film becomes porous, containing entrapped air that increases pigment-scattering efficiency by effectively lowering the refractive index of the surrounding medium. The air itself, as particulate matter in contact with the higher refractive index binder, contributes to light scattering. Thus, if the curves of Fig. 14 were extended to a sufficiently high PVC, the hiding power of the film would begin to rise again

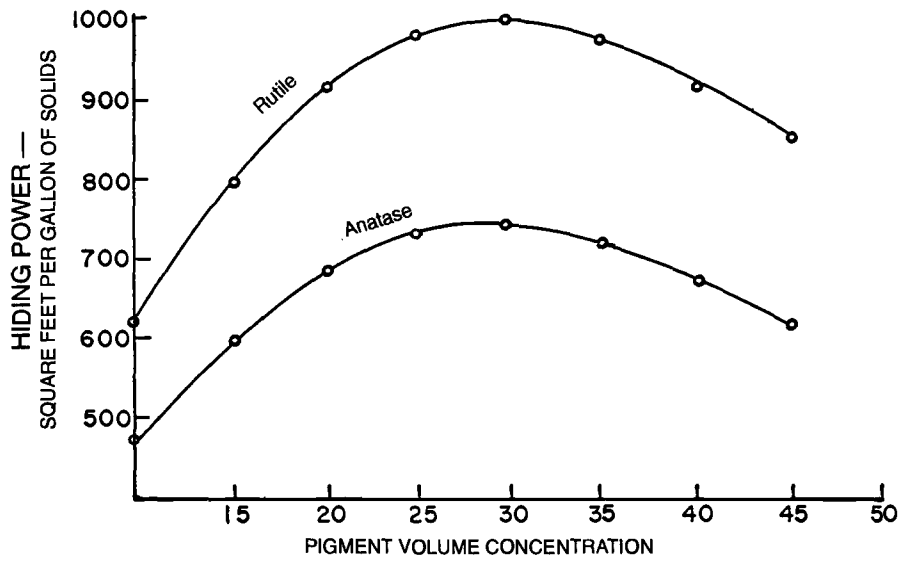

FIG. 14–Hiding power $H_{0.98}$ (ft²/gal) of solids at various PVC levels.

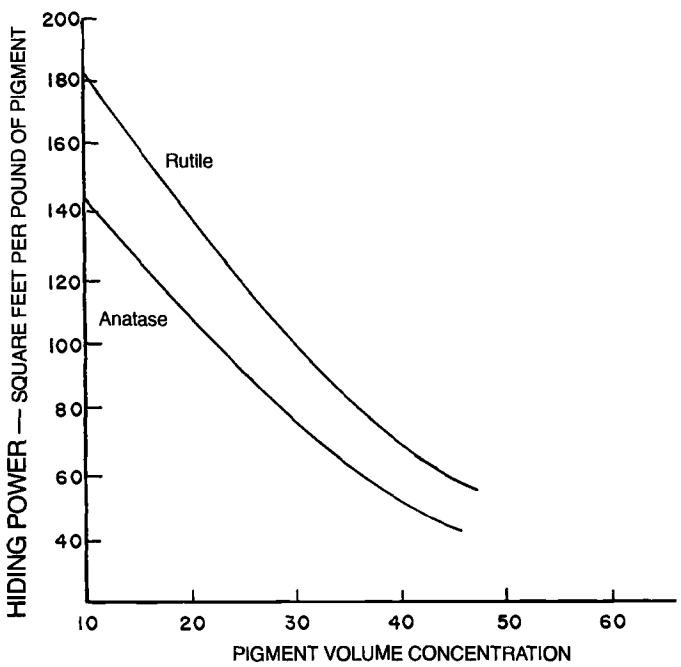

FIG. 15–Hiding power $H_{0.98}$ (ft²/lb) of pigment at various PVC levels.

due to the opacification effect of film porosity. Obviously this is an extremely impractical use of expensive titanium dioxide with no relation to actual formulation practice. However, porosity does in practice make a major contribution to hiding power in the important interior flat wall paint sector. In paints of that type, inexpensive inert white pigments are included in the formulation along with titanium dioxide for the esthetic purpose of producing a flat finish and to contribute hiding power by means of porosity. Stieg and Ensminger [*38*] showed that with paints over the CPVC that contain both TiO_2 and extender, hiding power is in a straight-line relationship with the Porosity Index (P.I.), with the slope of the line depending on the percentage of prime pigment and the nature of the extender. The Porosity Index is calculated from the equation

$$\text{P.I.} = 1 - \frac{\text{CPVC}(1 - \text{PVC})}{\text{PVC}(1 - \text{CPVC})} \tag{57}$$

The low-cost hiding power obtained from porosity is unfortunately accompanied by a deterioration in the quality of the film as manifested by poor scrub, soilant, and stain resistance. This is due to an insufficiency of binder, resulting in an air phase continuum that gives ready capillary access to staining materials.

10. MICROVOIDS FOR WHITE HIDING POWER

Through the use of encapsulated preformed microvoids, it has been found possible to obtain some of the hiding power benefit of entrapped air while avoiding or minimizing the deleterious effect of film porosity. The microvoids are supplied as a water dispersion of hollow beads having a plastic outer shell and water-filled core. Incorporated into a latex paint, the water in the core evaporates during the drying of the film and is replaced by air that functions as light-scattering particulates shielded from staining penetrants by the surrounding plastic shell. Because the microvoids alone are not able to produce the desired level of opacity in a film of normal thickness, the inclusion of titanium dioxide pigments in the paint formulation along with microvoids is essential. One widely used microvoid bead product is referred to as "opaque polymer" and employs a shell of thermoplastic polystyrene. Another type is a vesiculated bead in which titanium dioxide and water-filled "vesicles" are associated in a cross-linked polyester/styrene matrix. By using such products to partially replace titanium dioxide pigment, raw material cost savings have been demonstrated with no loss in film integrity or hiding power [*35,40*].

11. FORMAL HIDING POWER METHODS

a. ASTM Methods

D 344: Test Method for Relative Dry Hiding Power of Paints by the Visual Evaluation of Brushouts

This is essentially the same as the Krebs Method described in 4.d, differing only in requiring black-and-white instead of grey-and-white charts and in permitting checkerboard or other suitable contrast designs as well as the diamond-stripe pattern. Modern charts are 0.1 m^2 in area (1.076 ft^2) instead of 1 ft^2 as specified originally. Provision is made for reporting results in m^2/L as well as ft^2/gal.

D 2805: Test Method for Hiding Power of Paints by Reflectometry

This was adopted in 1969 and is actually a combination of two earlier methods, D 1738 and D 2614, that differed only in technique. It conforms with the general Kubelka-Munk method described in 8.e but is designed specifically for air-dried coatings. Originally it provided for the use of either black glass or charts for determining H_x and R_0. In later versions black glass is mandatory. R_∞ is determined by a separate application as described in 8.e.(1). The need for two test applications does not represent a significant extra effort since only the application on black glass requires the time-consuming spreading rate determination. The latter is accomplished by placing a template of predetermined area on the dry film, scraping off and discarding the film outside the confines of the template, then carefully scraping off the remaining film in the defined test area and weighing it on an analytical balance. The spreading rate is then calculated from the density and nonvolatile content of the paint using Eq 26. Having obtained the experimental values: R_0, H_x, and R_∞, the scattering coefficients and hiding power $H_{0.98}$ of the paint are calculated from these values using the Kubelka-Munk sequence shown in 8.e.(3) thus: $P_x = f(R_0, R_\infty)$, $S = P_x H_x$, $P_c = f(C; R_\infty)$, $H_c = P_c/S$ for $C = 0.98$. These calculation steps can be carried out individually or combined into the previously described computer program identified as Eq. 47: INPUT: R_∞, R_0, H_x, C—OUTPUT: S, H_c.

The method also provides for calculating the contrast ratio C_H at a specified spreading rate H, using the same experimental results but with a slightly different equation sequence as described in 8.e.(4), thus: $P_x = f(R_0, R_\infty)$, $S = P_x H_x$, $P_H = S/H$, $C_H = f(P_H, R_\infty)$. This sequence is summarized in the computer program identified as Eq 51: INPUT: R_0, H_x, R_∞, H—OUTPUT: S, C_H.

Earlier versions of D 2805 and its predecessor standards included or referenced the Mitton tables and graphs described in 8.g for solving the *K-M* equations. The method can be adjusted by appropriate experimental modifications to the measurement of baked enamels on black-painted metal panels as discussed in 7.d, or to other types of coatings and test substrates.

D 5007: Test Method for Wet-to-Dry Hiding Change

This is a rapid visual test designed to measure percent change in hiding power during drying. The paint is drawn down on a black-and-white test chart using a special multinotch applicator (Fig. 16) having eight notches with clearances in geometric progression ranging from 67 to 264 μm (2.65 to 10.4 mils). The clearance corresponding to an agreed visual endpoint (see 2.a) is estimated immediately after application and again after drying. The ratio of the two clearances multiplied by 100 gives the percentage change in hiding power:

$$\frac{\text{CLEARANCE}_{\text{WET ENDPOINT}}}{\text{CLEARANCE}_{\text{DRY ENDPOINT}}} = \frac{\text{WFT}_{\text{WET ENDPOINT}}}{\text{WFT}_{\text{DRY ENDPOINT}}} = \frac{\text{SPREADING RATE}_{\text{DRY ENDPOINT}}}{\text{SPREADING RATE}_{\text{WET ENDPOINT}}}$$

The equation assumes that, for any one drawdown, the ratio of clearance to WFT for the several notches does not deviate appreciably. On that basis WFT variations due to application technique or paint rheology would not affect the final test result. This is not a precision test but provides significant information of a practical nature with minimal effort.

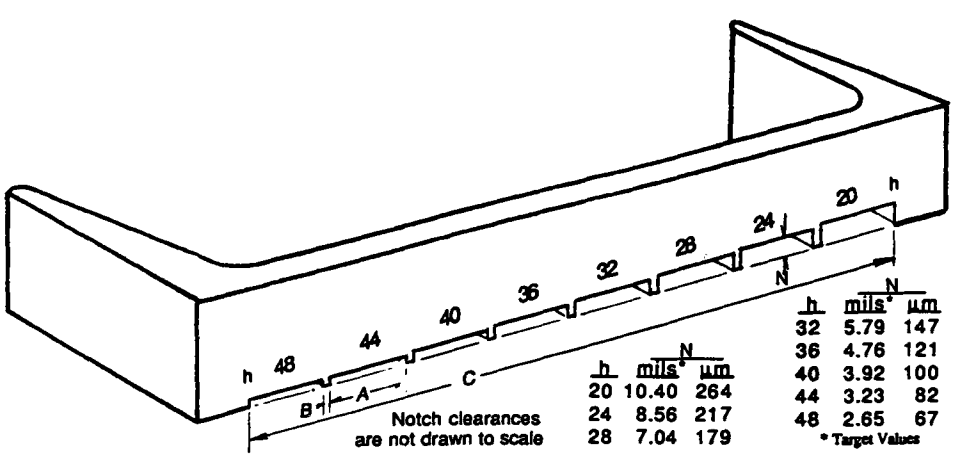

FIG. 16–Multi-notch applicator for ASTM D 5007.

D 5150: Test Method for Hiding Power of Architectural Paints Applied By Roller

This is a visual comparison method designed for use with interior wall finishes and intended to provide practical information from tests performed on a convenient laboratory scale. The test substrate is a large, sealed paper test chart (Fig. 17) with a series of stripes numbered 1 through 6 on a white background. The stripes range in shade from very light grey to black and were selected so that the color difference ΔE^*_{ab} between each successive stripe and the white surround is in a geometric progression from 2 to 64 CIELAB units. The dimensions of the test area are 24 by 36 in. = 6 ft^2 (610 by 914 mm = 5575 cm^2), sufficiently large to simulate practical application of paints with a roller. The paint is applied at a specified, controlled spreading rate, and the hiding power is reported as the stripe number of the darkest stripe perceived as being completely obscured. The concept of this test is that in practical applications the levelness of the paint film and hence its effective opacity is affected by the rheological properties of the paint. Thus, in practice paints tend to have lower hiding power than indicated by more customary test methods in which films are applied with maximum uniformity using a blade-type applicator. Relative practical hiding power among paints can be influenced for that same reason.

b. U.S. Federal Test Method Std. 141

Method 4121, Contrast Ratio at a Specified Spreading Rate

This pass-fail test was previously described in some detail in 5.f. Paint films are applied on black-and-white charts by brush or drawdown, and spreading rates are determined by a typical weight-area-density procedure, discussed in 6.b. CR values are plotted at several spreading rates to obtain graphically the CR at a specified spreading rate. For the test paint to pass, the CR at the specified spreading rate must have a specified minimum value.

Method 4122, Contrast Ratio at a Specified Dry Film Thickness on Black and White Glass Panels

An applicator is selected to obtain precisely the desired dry film thickness, the latter being measured with a micrometer to the nearest 0.0001 in. Separate drawdowns are made on black and white glass panels. Reflectances R_B and R_W are measured and the CR calculated. This is a simplistic concept in view of the undoubted difficulty in obtaining, measuring, and then repeatedly applying a precise predetermined dry film thickness.

c. ISO (International Standardization Organization) Methods

ISO 2814, Contrast Ratio (CR) at a Nominal Spreading Rate (SR) of 20 m^2/L on Black-and-White Charts or Polyester Film

A paint film is applied with a 100-μm clearance applicator to give a nominal wet film thickness of 50 μm, corresponding to a spreading rate of 20 m^2/L. Black and white substrate reflectances are measured and the contrast ratio calculated without a determination of actual spreading rate. Films cast on a clear polyester are measured, as described in 7.b, by placing the film alternately on black and white glass. Because different paints and application techniques with the same applicator give films differing significantly in thickness, the method is satisfactory only as a rough guide for paints of the same type and color evaluated by one operator.

ISO 3905, Contrast Ratio (CR) at a Spreading Rate (SR) of Precisely 20 m^2/L on Black and White Charts

This method, like ISO 2814, is intended to measure the CR at 20 m^2/L, but the *SR* in this case is determined carefully. Drawdowns are made with three applicators to obtain no-

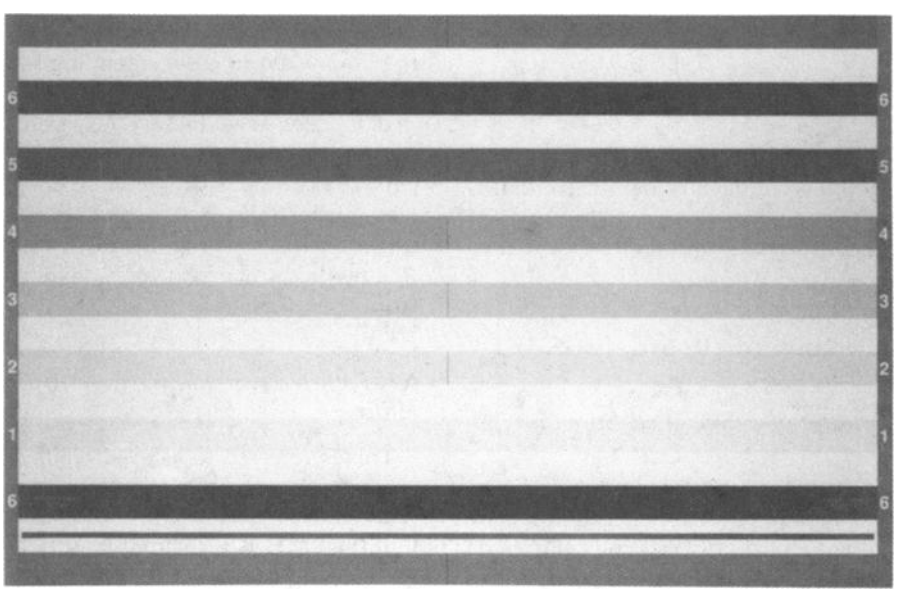

FIG. 17—Large gray scale chart (6 ft,^{2} 5575 cm^2) for roller application tests per ASTM D 5150.

minal wet film thicknesses of 40, 50, and 60 μm corresponding to SRs of 25, 20, and 16.67 m^2/L. After drying, the CR values are measured and the SR values determined by a typical weight-area-density method as discussed in 6.b. The dry film weight is determined as the difference between the painted and unpainted chart, with considerable precautions taken, as discussed in 7.a to avoid error due to nonuniform chart weight. A graph of CR versus SR is prepared on square-ruled paper from which the CR at exactly 20 m^2/L is determined by interpolation. The method is restricted to paints with a reflectance value of at least 25%. Weaknesses of this method are: (a) it fails to correct for possible variations in the reflectance of the white substrate, as discussed in 1.f; (b) the specified SR of 20 m^2/L corresponds to a wet film thickness of only 50 μm (2 mils), at which thickness irregularities in the surface of paper test charts can have an appreciable effect.

ISO 3906, Contrast Ratio (CR) at a Spreading Rate (SR) of Precisely 20 m^2/L on Polyester Film

This method is essentially the same as ISO 3905, differing only in the use of polyester film instead of black-and-white charts. Like ISO 3905, the method fails to correct for deviations in the white substrate from the ideal reflectance of 80%. However, the problem of surface irregularity is largely overcome due to the superior levelness of the plastic film. Since true hiding power is a spreading rate, neither this method nor ISO 3904 or ISO 3905 measure hiding power as such.

ISO 6504, Kubelka-Munk Method for White and Light-Colored Paints

This is in accordance with the general *K-M* hiding power method described in 8.e. It calls for an all-black substrate which can be glass or polyester film over black glass. The Mitton graph and table described in 8.g are included, which makes it very similar to early versions of ASTM D 2805.

d. British Standards Institute, BSI 3900

Part D4. Comparison of Contrast Ratio of Paints of the Same Type and Color—This method is technically identical with ISO 2814 (11.c).

Part D6. Contrast Ratio at 20 m^2/L Using Polyester Film—This method is technically identical with ISO 3906-1980 (11.c).

Part D7. True Hiding Power (SR at C = 0.98) by the Kubelka-Munk Method—This method is technically identical with ISO 6504 (11.c) and in accordance with early versions of ASTM D 2805 and the general *K-M* hiding power method described in 8.e.

e. Canadian General Standards Board, (CGSB) 1-GP-71

Method 14.1, Visual Hiding at a Specified Spreading Rate

The test substrates are black-and-white or black-and-gray checkerboard charts with an area of 0.1 m^2. The appropriate chart is specified according to a list of CGSB color numbers, with black-and-gray being used for lighter colors. The paint is applied by brush or drawdown. In brush application the SR is controlled accurately by weighing container and brush before and after application, with a specified volume being delivered to the chart surface by syringe. With drawdowns, presumedly identical applications are made on glass and charts and the WFT determined on glass by means of an Interchemical (ASTM D 1212) wet film thickness gage. For the test paint to pass, the dry paint film is required to completely obscure the contrast pattern of the chart.

Method 14.2, Spreading Rate Determined at Full Visual Hiding (for Quick-Drying Coatings)

Successive thin coats are applied by spraying onto black-and-gray or black-and-white charts until visual hiding of the dry film is complete. The SR is calculated from the difference in weight of the coated and uncoated chart. This can be expressed in m^2/kg of dry film or m^2/L of the original liquid coating.

Method 14.7, Contrast Ratio on Black and White Glass Panels at a Given Spreading Rate or Dry Film Thickness

This is modeled after the NYPC method described in 5.d. WFT is determined with an Interchemical gage or DFT with a micrometer. The target film thickness is bracketed experimentally to obtain two points on a CR versus reciprocal film thickness graph and the CR at the target thickness determined by interpolation. The experimental CR values are corrected for $W = 0.80$ before plotting the graph.

f. French Standards Association (AFNOR)

NF-T30-075, Spreading Rate at a Contrast Ratio (CR) of 0.98

Paint films are cast on clear polyester at several thicknesses and CR values determined after drying by measuring reflectances over a black-and-white substrate. Dry films just below and above 0.98 in CR are measured by weight or micrometer to obtain experimental spreading rates in m^2/kg or m^2/L and results interpolated to obtain the spreading rate at exactly CR = 0.98. The introductory text points out that this method measures true hiding power in preference to ISO 3905 and 3906 (11.c) which simply compare CR values at 20 m^2/L. It also refers to the experimental film thickness not being limited to 50 μm as in the ISO methods. No provision is made in this method to correct for deviations of the white substrate from $W = 0.80$.

NF-T30-076, Spreading Rate at Complete Visual Hiding

This is referred to as a "simplified" method. Several films are cast on polyester to obtain one that shows full hiding when placed over a black-and-white background. The dry film thickness is measured by difference with a micrometer and the hiding power calculated in m^2/L. Potential users should consider whether this method, though simple in concept, might be excessively burdensome in execution.

g. German Standards Institute (DIN)

DIN 53162, Hiding Power of Air Drying Nonchromatic Paints

This is a Kubelka-Munk method which is essentially the same as ISO 6504, but includes auxiliary test procedures for measuring paint density and nonvolatile content. The Mitton nomograph and table (8.g) are employed.

DIN 53164, Relative Scattering Power of White (TiO_2) Pigments

This method measures the Kubelka-Munk scattering coefficient S of a TiO_2 pigment and reports its value as a percentage of the scattering coefficient of a reference pigment measured in the same way. The determination of S is based on the solution of Eq 44: $P = f(R_0, R_\infty)$ using the Mitton nomograph. The method calls for the test pigment to be dispersed in an alkyd or a plasticized polyvinyl chloride vehicle. R_∞ is measured from a thick, full hiding film of the dispersion and R_0 from a nonopaque film applied on a black plastic substrate. The spreading rate H_x of the pigment is determined in a unique way, by igniting a known area of film on plastic and weighing the residue. This method is basically the same as DIN 53162 and other *K-M* methods (8.e), with the difference that only relative values are reported. There is no attempt to report actual scattering coefficients or to calculate hiding power in physical units, although this could easily be done on the basis of the accumulated data.

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Mass Color and Tinting Strength of Pigments

by Julio I. Aviles[1]

DEFINITIONS

The mass color (MC) of a coating is defined in ASTM Terminology Relating to Paint, Varnish, Lacquer, and Related Products (D 16) as:

> "the color, when viewed by diffuse reflected light, of a pigment-vehicle mixture of such thickness as to obscure completely the background. Sometimes called over-tone or mass-tone."

Mass color is produced by the reflected light (R_∞ at infinite thickness) of an opaque coating and depends on the pigment concentration, degree of dispersion, coating thickness, and the light absorption (K) and scattering (S) of pigments and binders. Mass color is applicable to both chromatic and achromatic pigments.

Other definitions of interest, taken from ASTM Terminology of Appearance (E 284), are as follows:

- Brightness is an "aspect of visual perception whereby an area appears to emit more or less light."
- Chroma is the attribute of color used to indicate the degree of departure of the color from a gray of the same lightness. Chromatic is a term meaning "perceived as having a hue; not white or black."
- CIE 1931 standard colorimetric system is "a system for determining the tristimulus values of any spectral power distribution using a set of reference color stimuli X, Y, A and the three CIE color-matching functions $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, $\bar{z}(\lambda)$ adopted by the CIE in 1931."
- Colour Index is a listing of colors by name and number by The Society of Dyers and Colourists, London, 1987. It is available from the American Association of Textile Chemists and Colorists, P.O. Box 12215, Research Triangle Park, NC 27709.
- Hue is "the attribute of color perception by means of which a color is judged to be red, orange, yellow, green, blue, purple, or intermediate between pairs of these, considered in a close ring."
- Lightness is "(1) the attribute of color perception by which a nonself-luminous body is judged to reflect more or less light." "(2) the attribute by which a perceived color is judged to be equivalent to one of a series of grays ranging from black to white."
- Masstone is a pigment-vehicle mixture that contains a single colorant only. This definition includes certain colorants that may contain more than one pigment but are tested and used as if they contain only a single pigment.
- Saturation is "the attribute of a visual sensation that permits a judgment to be made of the proportion of pure chromatic color in the total sensation." Saturation can also be described in a mathematical manner as in ASTM E 284.
- Scattering is "the process by which light or other electromagnetic radiant flux passing through matter is redirected over a range of angles."
- Shade is "a color produced by a dye or pigment mixture including black dye or pigment."
- Tint is "a color produced by the mixture of white pigment or paint with a chromatic pigment or paint."
- Tristimulus values are "the amounts of three specified stimuli required to match a color." In the CIE system, these stimuli are assigned the symbols X, Y, and Z.

TINTING STRENGTH

Tinting strength is a measure of the effectiveness with which a unit quantity of a colorant changes the color of a material (ASTM E 284). It may be thought of as a pigment's "coloring power." For those colorants that both scatter and absorb, the scattering and absorption tinting strengths must be specified. ASTM D 284 defines scattering tinting strength as "the relative change in the scattering properties of a standard black material (with no scattering colorant present) when a specified amount of a white or chromatic scattering colorant is added to it" and absorption tinting strength as the relative change in the absorption properties of a standard white material when a specified amount of an absorbing colorant, black or chromatic, is added to it."

Pigment concentration is important to coating strength and cost, and therefore tinting strength can be an important relative economic value factor in selecting one paint over another. There is no particular value of tinting strength that can be stated as desirable unless an end use is stated. In certain cases a high value is desirable and in others a low value is needed to achieve a desired color/strength effect. In a general sense, tinting strength is determined by dilution of a test paint and a reference paint with a standard "mixing white paint" in the case of chromatic paints or a standard "tinting color" in the case of white paints, drawing down the resulting pastes on a suitable substrate, and then instrumentally measuring tristimulus values or visually comparing the specimens. The latter comparison technique has lower precision than the former. Details for the preparation of a standard

[1]Senior technical service representative, Kronos Inc., Wyckoffs Mill Road, Hightstown, NJ 08520.

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mixing white paint are described in ASTM Test Methods for Relative Lightfastness of Pigments Used in Artists' Paints (D 4303) or a commercial titanium-dioxide white artists' paint may be used. It should be understood that the mixing white paint must be made with the same vehicle type—acrylic, alkyd, or oil—as the paint to be tested.

In color tints, differences in gloss and haze may be mistaken for a lighter tint or lower tinting strength than really exists. In grays, these factors may be interpreted as higher white pigment strength than exists. Instruments cannot compensate for specular gloss or haze differences between a sample and a standard, and this can result in erroneous tint strengths. It is possible to equalize gloss differences between the specimens by top coating with a clear coating. Evaluation through the clear coating reveals the true tinting strength differences between sample and standard.

Tinting strength results can also be affected if the lightness, chroma, and saturation of the sample differ significantly from those of the standard, since this involves matching two color variables, lightness and chroma or lightness and saturation, by adjusting only the amount of pigment used [*1,2*].

Chromatic Paints

ASTM Test Method for Determining the Relative Tinting Strength of Chromatic Paints (D 4838) is a method used for determining the absorption tinting strength of a chromatic (define) test paint relative to that of a paint of the same chemical type. The method is intended for comparison of paints that contain the same chemical type vehicle (acrylic, alkyd, or oil) and single-pigment colorants of the same Colour Index name and number. Knowledge about the amount of pigment and other components of the paint is not necessary.

The color measuring instrument can be either a spectrophotometer that provides 1931 CIE tristimulus values X, Y, Z for CIE standard illuminant C, or a tristimulus colorimeter providing either such tristimulus values or colorimeter readings R, G, B. Other related test methods useful in following ASTM D 4838 are ASTM Test Method for Computing the Colors of Objects by Using the CIE System (E 308) and ASTM Practice for Obtaining Spectrophotometric Data for Object-Color Evaluation (E 1164).

ASTM Test Method for Color and Strength of Color Pigments with a Mechanical Muller (D 387) is used for comparing the color and strength of a pigment with a reference standard of the same type. The test method is not to be used with white pigments. The pigments are dispersed in a suitable vehicle with a mechanical muller. Opaque drawdowns are made on white paper charts that have a black band and a surface that is impervious to paint liquids. These are then compared either visually or instrumentally for color and strength differences.

White Paints

ASTM Test Method for Relative Tinting Strength of White Pigments by Reflectance Measurements (D 2745) is a procedure for determining the relative tinting strength of white pigments by reflectance measurements made on black tints. It is only applicable for comparing a test pigment with a reference standard. The method is conducted by dispersing the pigment in an agreed on solvent-free vehicle and then letting it down with additional vehicle that has been tinted with a lamp black that has been predispersed in a vehicle similar in nature to the test vehicle. Refined or low-bodied linseed oil should not be used. Both dispersion and let-down are achieved with an automatic, mechanical muller. Tristimulus values are determined with a colorimeter.

ASTM Test Method for Relative Tinting Strength of White Pigments by Visual Observation (D 332) is a procedure for determining the relative tinting strength of white pigments by visual evaluation of blue tints. It is only applicable for comparing a test pigment with a reference standard. Specified amounts of white pigment and a blue tinting pigment that conforms to ASTM Specification for Ultramarine Blue Pigment (D 262) are dispersed together in a refined linseed oil with an acid number of about 4 using a glass hand muller or an automatic muller. The pastes are drawn down together on a panel and visually evaluated for tinting strength. A numerical rating of tinting strength is obtained by preparing dispersions with the standard white pigment and more or less of the tinting pigment and comparing them until the lightness of the test paste is matched. The weight of the tinting pigment is used to calculate the relative tinting strength.

PIGMENT DISPERSION

Mass color and tinting strength require that the pigments be well dispersed in the binder to achieve maximum tinting strength. Ideally, it would be desirable to break down pigment agglomerates to individual particles, i.e., to an ultimate dispersion state. However, in actual practice this would be difficult, if not impossible, to achieve. Therefore, pigments under investigation for MC and TS must be processed in the same manner and receive the same level of mechanical work. Mechanical mullers, Fig. 1, which are instruments that have two circular, usually ground, glass-grinding surfaces that contain the pigment and vehicle, are used for dispersing the two components. (A satisfactory muller is supplied by the Hoover Color Corp., 13 Cordier St., Irvington, NJ 07111.) Development of tinting strength is dependent on the force applied to the glass plates, the number of revolutions used, and the mass of pigment and of vehicle used. If muller conditions, pigment, and vehicle have not been agreed on by purchaser and seller, the mandatory dispersing conditions given in the Annex of ASTM D 387 should be used to achieve the maximum level of tinting strength. These conditions include:

- Determination of the appropriate ratio of color pigment to dispersing vehicle for the standard and test pigments.
- Determination of appropriate masses of pigment and vehicle to use.
- Preparation of a standard tint by application of 100 lb to the muller plates, introducing the appropriate mass of pigment/vehicle, and mulling the paste for 100 revolutions in two stages of 50 revolutions each. This is then repeated on three more specimens of the standard mixture except the mulling is carried out for 200, 300, and 400 revolutions in stages of 50 revolutions.
- Each of the four specimens is compared one to the other for tinting strength, and the minimum number of revolutions

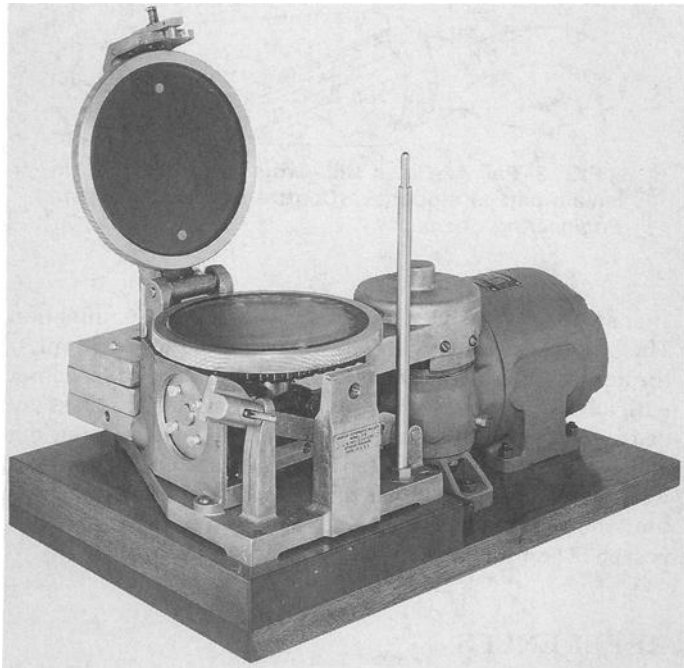

FIG. 1—Hoover Automatic Muller. *Automatic* means motor driven. (Courtesy of Hoover Color Corp.)

needed to develop maximum or full tinting strength is determined.

Parameters to record and the dispersing conditions for three pigments used in an interlaboratory test to determine the precision of this standard method are given in Table 1.

PIGMENT-DISPERSION TECHNIQUES

It should be kept in mind that the techniques described in this chapter pertain to preparing specimens for determination of tinting strength, mass color, etc., and are not meant for pigment dispersion in general. The general topic of pigment dispersion is discussed elsewhere in this manual as well as in numerous references [3–7]. There is a vast amount of literature that deals with the surface treatment of organic pigments to improve ease of dispersibility, and interested readers are encouraged to seek such information in the classic work of Hayes [*8*] as well as others [*9–11*]. Detail about the surface treatment of inorganic pigments is also in the literature [*12–14*]. Much of the following information is abridged and modified from the chapter with the same title in the previous edition of this manual [*15*].

Spatula and Hand Muller

Grinding pigment/vehicle combinations can be done with a spatula or a hand muller by rubbing or mulling the materials over a 3 by 12-in. (8 by 30-cm) strip area on a glass plate, Fig. 2. The rubbing is done by pushing the muller up one side and pulling it down the other side of the strip area so all color particles receive the same amount of rubbing. One rub is one up and down course. Early studies by Ayers [*16*] indicated that a muller gave more reliable results than a spatula and that the rubbing surface may vary a great deal without affecting the results. Stutz's [*17*] results during investigation of the tinting strength of white pigments also found a muller superior to a spatula. It was also found that a weighted or unweighted muller can be used without affecting the results.

AUTOMATIC MULLERS

Automatic or mechanical mullers have two circular glass-grinding surfaces that contain the pigment/vehicle paste. The grinding surfaces are usually constructed of ground glass with one stationary and weighted to exert a pressure of 100 psi (440 N) and the other rotary with rotation effected by a motor. Because rotation is about the disk centers, paste at the center can receive less mulling than paste located near the edges. To compensate for this effect, it has been found helpful to spread the paste in a ring approximately halfway between the edge and center. The revolutions per mulling cycle can be adjusted in increments of 1 to 999. Mechanical muller advantages include very good development of tinting strength, possibility to rapidly mull small quantities of materials, and efficient processing of a large number of samples.

The Annex of ASTM D 387, briefly described above, has a specific way to operate an automatic muller when determining tinting strength or mass color.

Laboratory Miniature Media Mills

There are commercial horizontal or vertical laboratory media mills that can process up to a quart of millbase. For small grinds, a media mill can be simulated with a laboratory dispenser equipped with a fiber or Teflon® 1⅝-in. disk, a 200-mL tall-form beak, and media. Equal volumes of millbase to media are used. Grinds may be 60.0 g for carbon black and some organics to 160.0 g for inorganic pigments. The millbase must be prepared carefully to eliminate gross and oversized agglomerates. Peripheral impeller speed should be 2000 ft (610 m) per minute, and the mixture should be ground for a set time or to a set dispersion level such as Hegman value 7.0+. Advantages of media mills include development of the

TABLE 1—Interlaboratory pigment dispersing parameters and specific conditions obtained for maximum tinting strength (data taken from ASTM D 387).

Parameter	Pigment Type		
	Yellow Iron Oxide	BON Red	Pthalocyanine Green
Force applied, lb (N)	100 (440)	100 (440)	100 (440)
Total no. revolutions	100 (2 × 50)	200 (4 × 50)	400 (8 × 50)
Mass of color pigment, g	1.0	0.6	0.75
Mass of dispersing vehicle, g	1.7	1.4	1.8

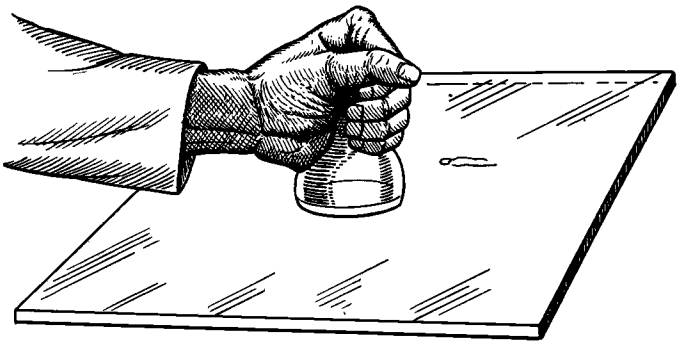

FIG. 2–Rubbing pigment and vehicle with glass muller and slab.

highest mass color and tinting strength, simulation of actual factory grinding conditions, and low cost.

Laboratory Roller Mill

Small three-roller mills have been found useful for grinding small, laboratory-size batches of paint. Rolls of such mills are about 4 in. (10.16 cm) in diameter and 8 in. (20.82 cm) in length. Batches as small as 5 g have been prepared in such mills.

Pall Glass Mill

Metal-free, small quantities of pigment paste have been prepared with the Pall Glass Mill [*18*], which is depicted in Fig. 3. It is a heavy ground-glass stopper in a heavy glass joint. The mixed, unground materials (1 to 8 g) are placed in the joint, and the stopper/plunger is inserted. The stopper is rotated with a small motor at about 150 r/min. In this mill, grinding pressure ranges from 20 to 30 psi. The Pall Glass Mill is said to be an improvement over hand mulling because it saves time and because it results in greater development of tinting strength.

PIGMENT CONCENTRATION

Paste viscosity has an effect on grinding efficiency, and it determines the level of mass color and tinting strength that is developed. Ayers [*16*] investigated iron oxides, and the results indicated that color developed faster as paste viscosity increased. A low-viscosity paste had a reflectance of 26% at a wavelength of 700 nm, whereas high-viscosity paste was darker and redder with a reflectance of 23%. There is a point above which viscosity has no effect.

MIXING TIME OF LIQUID COLORS

One of the properties of oil or universal liquid colorants is the ease with which they can be incorporated into white paints. A method for testing the speed of incorporation has been described by Paul and Diehlman [*19*]. This method involves use of a mechanical rotating bottle that contains a white paint, the liquid colorant, and a grinding media. When the test was first developed, No. 11 lead shot was used; however, today glass beads, zirconia grinding media, and steel

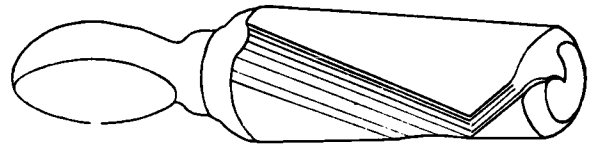

FIG. 3–Pall All-Glass Mill. Grooved plug rotates in female part of stopcock. (Courtesy of *Industrial and Engineering Chemistry.*)

shot are among the media used to avoid lead contamination. The bottle is charged with 550 g of grinding media, 2 mL of the liquid colorant, and 75 mL of white paint. It is then closed with a cork, concave on the inner end to match the glass end of the bottle, and placed in the holder of the rotating machine. The bottle is then tilted and rotated slightly by hand to wet the container walls. The mill is then mechanically rotated until the paint is homogenous in that no streaking of the color is seen. The time in seconds for mixing is determined.

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Part 11:
Physical and Mechanical Properties

44

Adhesion

by Gordon L. Nelson[1]

ORGANIC COATINGS ARE APPLIED to a variety of substrate materials (woods, metals, plastics, ceramics) for decorative, protective, and functional applications. In each case, it is imperative that the coating adheres well to the substrate. Accordingly, adhesion assessments should be an integral part of coating development. This may seem a straightforward task, but coating adhesion is, in fact, extremely complex and often poorly understood. The growing use of plastics to replace metals and other "traditional" materials renders the issue even more complex [*1–2*].

The objectives of this chapter are to review briefly salient concepts of the adhesion process and to discuss currently accepted standard test methods.

FUNDAMENTAL CONCEPTS

While the very definition of "adhesion" is of some controversy [*1*], adhesion may be loosely defined as the attraction between dissimilar bodies for one another. ASTM D 907 on Terminology of Adhesives defines adhesion as "The state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking action or both." In discussing adhesion assessment, one must consider the issue from two different aspects: *basic* adhesion and *practical* adhesion. Basic adhesion signifies the summation of all interfacial, intermolecular forces, whereas practical adhesion is used to represent the forces or work required to disrupt the adhering system [*3*]. The next section will be devoted to theories and concepts of basic adhesion and will of necessity be brief. The perspective will be from that of a polymeric coating on a plastic substrate [*2*]. Metal and metal oxide substrates will be discussed where appropriate. The reader is referred to Refs *4–7* for a more thorough discussion.

BASIC ADHESION

Work of Adhesion

Bonding between polymeric coatings and substrates may be viewed as the union of two contiguous polymer phases, one a solid and the other a liquid which solidifies to form a thin film. The reversible separation of the two phases may be expressed by the work of adhesion

$$W_a = Y_1 + Y_2 - Y_{12} \tag{1}$$

where W_a is the work of adhesion, and Y_1 and Y_2 are the surface tensions of the two phases. The maximum force per unit area, σ^2, to effect this process is the ideal adhesive strength [*8*]

$$\sigma^2 = [16/9\,(3)^{12}]\,(W_a/Z_0) \tag{2}$$

where Z_0 is the equilibrium separation between the two phases, usually about 5 Å. The average value W_a for polymers is typically 50 ergs/cm^2, yielding a theoretical value for σ^2 of 15 000 psi (103 mPa). For practical purposes this value is never attained, primarily due to the fact that perfect intermolecular contact is most unlikely. In fact, this is at least an order of magnitude higher than the practical adhesive strength usually observed. This deviation from ideality has led to the promulgation of several theories of adhesion, none of which are universally recognized [*9*]. This is not unexpected, since most theories deal exclusively with the mechanisms of bond formation and disregard the fact that bond strength is ultimately a function of both the degree of bond formation, the nature of the bond (chemical and physical), and the rheological properties of the bonding phases. The strength of an adhesive bond is, in fact, a function of all of these factors. Summary paragraphs about basic theories of adhesion follow below.

Fracture Theory

The area of interfacial bonding between coating and substrate will, in most instances, contain voids or defects. The result is deviation between the ideal adhesive strength and the practical limit.

Good [*10*] and Williams [*11*] have applied the theory of cohesive fracture to coating fracture. The concept that fracture propagates from the weakest point, a defect, is fundamental to fracture mechanics. The strength of a bond, in terms of the energy required to induce fracture, is described as a function of the defect size and the energy dissipated by irreversible processes (plastic deformation, light emission, and electric discharge). The general equation given is

$$f = k\,(EF/d)^{1/2} \tag{3}$$

where f is the fracture stress, $k = (4/\pi)^{1/2}$, E the elastic modulus of the material, d the defect length, and F the fracture energy or total work per unit area of fracture surface, which is dissipated. Accordingly, the fracture energy

$$f = W_a + W_i \tag{4}$$

[1]Dean, College of Science and Liberal Arts, Florida Institute of Technology, 150 West University Blvd., Melbourne, FL 32901-6988.

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where W_a is the work of adhesion and W_i is the total work for the irreversible processes. For all practical purposes W_i is much greater than W_a, therefore [*12–13*]

$$f = W_i \tag{5}$$

Weak Boundary Layer Theory

Proposed by several workers [*14–16*], the weak boundary layer theory maintains that true interfacial fracture does not occur, and that fracture usually occurs *cohesively* in a weak boundary layer (WBL), which may be near the interface between coating and substrate. Experimental evidence has perhaps disproved the first point [*10*], that true interfacial failure can occur, but it has been shown that the second is valid in some instances [*17-18*].

Of practical importance to WBL investigations is the locus of fracture, which can occur in one or more of the zones in Fig. 1. For a strong bond, the boundary layer (layers) must be rheologically sound and chemically durable. The zone of failure may, of course, be studied by SEM, TEM, and FT-IR. In fact, thin layers of coating have been noted where interfacial failure was only thought to occur on visual examination.

Wetting—Contact Theory

The wetting-contact theory states that van der Waals attractive forces alone provide sufficient coating/substrate bond strength given perfect molecular contact, and that the extent of contact and resulting bond strength are functions of wetting energetics [*20–28*]. No one denies the importance of wetting in adhesion, i.e., the lower the contact angles, the more the interfacial area of contact, which generally yields improved adhesion (Fig. 2).

However, thermodynamic wetting is a necessary but not sufficient condition for the establishment of coating film adhesion. Wetting is a kinetic phenomenon as well. Furthermore, this model does not consider the effects of weak boundary layers or the effects of defects or fracture mechanics. What is the effect of surface contamination on the contact angle?

Diffusion Theory

Voyutskii and others [*29–33*] have proposed that coating adhesion between high polymers arises from interdiffusion.

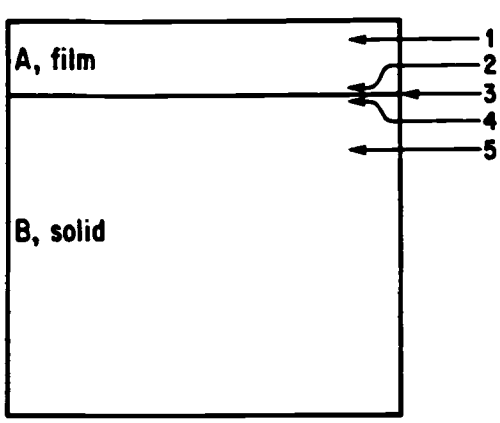


FIG. 1–Weak boundary layer theory. Possible zones of failure (after Good [*19*]).

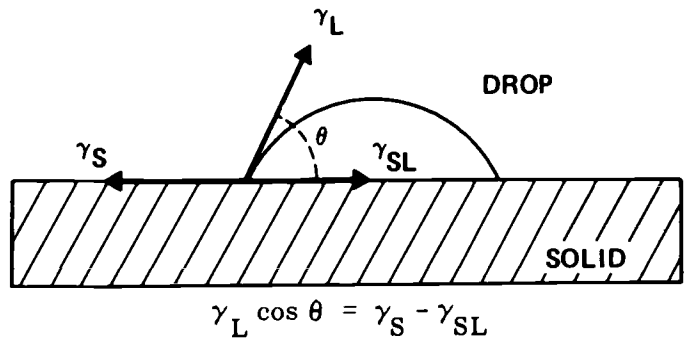


FIG. 2–Contact angle.

This has been validated somewhat by the observation that adhesive strength is a function of polymer molecular weight, structure, and contact time.

Key to this theory is the concept that no clear-cut interfacial boundary exists, but rather that an interphase exists which consists of polymer chain segments from both contiguous phases. The theory has been criticized for giving insufficient weight to the contribution of van der Waals attractive forces. Nevertheless, for the case of solvent-borne organic coatings applied to plastic substrates, this phenomenon is intuitively appealing.

Interdiffusion of coating and substrate polymer molecular segments is a function of polymer-polymer compatibility. An interphase forms as a result of the blending of the two phases. Although polymer pairs are generally incompatible, Helfand and others [*34–38*] have utilized statistical thermodynamics to predict that interdiffusion also occurs as a result of the tendency for free energy at the interface to minimize. A useful equation which describes interfacial thickness as a function of the Flory-Huggins interaction parameter as derived from Hansen solubility parameters is [*36,38*]

$$a_i = 2\,(m/x)^{1/2} \tag{6}$$

Where a_i is the interfacial thickness expressed as the cross sectional area of a lattice cell, m is a lattice constant directly proportional to nearest-neighbor contacts, and x is the Flory-Huggins interaction parameter. By this equation, interfacial thickness increases by interdiffusion as the solubility parameter difference between the two phases decreases. Although experimental verification is scarce, adhesive strength has been shown to decrease with increasing disparity in the solubility parameters of the two phases [*39*].

It is important to note that diffusion should occur in the latter stage of bond formation, the first stage being wetting to establish contact. Additional support for the theory comes from the observation that adhesive strength between certain high polymers increases with time [*30*]. This theory, however, cannot be applicable to systems involving one or more hard solids (metals, glass, or metal oxides).

Chemical Adhesion

The bond strength of covalent bonds is one to two orders of magnitude greater than van der Waals attractive forces. There have been numerous applications where interfacial chemical bonds have been employed to promote adhesion. Dramatic increases in bond strength have been reported [*40*].

Coupling agents such as chrome complexes [41], silanes [42], and titanates [43] have been used effectively. Organic functionalities, including isocyanates, carboxyls, amides, amines, hydroxyls, and epoxides [43–44], have been reacted interfacially to enhance adhesion.

Adhesive strength has been shown to increase with functional group concentration as expressed by

$$f = kC^n \tag{7}$$

where f is the adhesive strength, C the functional group concentration, and k and n are positive constants [45]. There, however, appears to be an upper limit for functional group concentration above which adhesion may tend to decrease [46–47].

Mechanical Adhesion

In mechanical adhesion substrate roughness is thought to provide a mechanical locking of the coating to the substrate. However, if there is not intimate contact between the coating and the substrate, then increased roughness should lead to a *decrease* in adhesion by producing uncoated voids. In the practical application of electroless metals on polymer substrates, etchants are used which create deep channels, increasing adhesion. Other examples are anchor coats for PTFE, adhesion to porous anodic films on aluminum, and hot melt polyolefin coatings on metals. Mechanical adhesion is also important for porous substrates such as wood, cloth, and paper. Since good adhesion can be obtained on smooth surfaces such as glass, questions can be raised about the general validity of the mechanical adhesion mechanism. It should also be noted that mechanical abrasive treatment of a solid surface may also yield macroradicals and active secondary chemical products, which if they do not come into contact with atmospheric oxygen, may interact with components of the coating. This has been shown for certain adhesives. Active radicals or functionality would yield adhesion, better described as mechanico-chemical adhesion than just mechanical [7,48–49].

Electrostatic Adhesion

In the theory of electrostatic adhesion, when two dissimilar materials are brought into contact, a charge transfer takes place which results in the formation of an electrical double layer, much like a capacitor. Work would then be required to separate the two charged layers. This is thought to be particularly applicable to metal-polymer bonds. Indeed, ionizing discharge has been shown to affect a copper to acrylic bond but not copper on salt (NaCl) or glass. This theory would not be applicable to two nonpolymer systems [49–50].

Acid-Base Adhesion

In the acid-base adhesion theory, it is said that the strength of the adhesive bonds is increased significantly by acid base interactions between coating and substrate. Appropriate modification of surface acidity or basicity of the substrate should increase adhesion. Modification of surface acidity or basicity of inorganic solids can increase mechanical properties (modulus, extension to break, and toughness) of coatings on these substrates. It has also been claimed that the reverse is true, however [51–52].

Combination of Phenomena

The preceding theories interpret adhesion in terms of single phenomena, each of which undoubtedly plays some role in interfacial bonding between coating and substrate. One should be cautioned, however, against exclusive use of a single theory to explain the adhesion of a given system. A more logical approach has been proposed by Allen [53]

$$\psi = a\psi_A + b\psi_B + c\psi_C + \ldots \tag{8}$$

which suggests that a combination of phenomena is more realistic, that is, that basic adhesion is the summation of *all* interatomic or intermolecular interactions at the interface. One would think that systematic studies could be made to assess the contribution of a given variable to the adhesion process, with the others being held constant. This would reveal useful information as to factors critical to coating adhesion for a particular system. Unfortunately, being able to accomplish that task is questionable given that adhesion assessment not only involves factors of basic adhesion but variation in application of the applied external stress (tensile, shear, or peal) and many other factors.

It can be concluded that adhesion is an interfacial phenomenon in which both physical and chemical forces operate when surfaces develop to form an interface. Adhesive strength is a measure of the degree to which the two surfaces are attracted. This is a function of wettability, relative surface energetics of both phases, and of the kinetics of wetting. For integrity of a bond at the interface between a coating and a substrate, one needs to consider the following factors:

1. Thermodynamics and kinetics of the formation of the bond.
2. The forces acting near the interface in both the coating and the substrate.
3. The cohesive forces within the coating layer.
4. Internal stresses in the coating layer.
5. The behavior of the coating layer under stress.

To understand basic adhesion one must understand the surface chemistry, surface physics, surface architecture, coating polymer chemistry and physics, polymer rheology, coating internal stresses, fracture mechanics, and effects of changes in the environment. In fact, it has been noted that spontaneous loss of adhesion can occur due solely to internal strain of the coating [54–56].

Effects of Substrates

Additional Chemistry

The adhesion of organic coatings to metals is at a high level of development in the practical sense. The contribution of surface energy, chemical functionality, surface irregularities, and contaminants (oxides, adsorbed water, etc.) have been identified.

On the other hand, coating adhesion to plastic substrates has presented additional complexities. Polymer surfaces are often more difficult to wet and bond because of low surface energy, incompatibility, chemical inertness, or the presence of contaminants (oils, lubricants, plasticizers, etc.), and weak

boundary layers. Surface modification techniques have been developed to enhance adhesion. In the absence of surface preparation, coating adhesion is felt to be a function primarily of van der Waals and/or polar-dipolar attractive forces, mechanical adhesion (from surface irregularities), and interdiffusion. This latter contribution to adhesion has been studied using scanning electron microscopy. In Fig. 3 is presented a scanning electron micrograph of a thermoplastic acrylic coating applied to modified polyphenylene oxide (a blend of PPO and polystyrene), an important engineering thermoplastic. The first coating contains 60% of the recommended amount of solvent. The interface formed is sharp and well-defined. In this instance, adhesion appears to be due largely to mechanical and attractive forces. Figure 4 shows the same substrate and coating, which in this case contains 100% of the recommended amount of solvent. The sharp interface seen in Fig. 3 is no longer present, an intermediate zone or interphase having formed in its place. Diffuse interface formation of this magnitude is undoubtedly unique to coatings applied to plastics. Bond strength will be a function of formulation, solvent content, and drying time [*2*].

Organic coatings are complex formulations; thus, the polymer chemistry at the developing coating substrate interface will clearly be impacted by the solid surface, whether plastic, metal, or inorganic, that is, the polymer interface may be somewhat different than the bulk coating (i.e., a boundary layer). Fully developed coatings may also be porous or permeable, thus aging and weathering may impact adhesion, as water, oxygen, and other agents penetrate to the polymer coating solid interface [*7,57*]. Indeed, some coatings that have acceptable adhesion while dry may fail badly when tested under high humidity or after immersion in water for several hours.

It has been shown for polyolefin-metal adhesion that oxidation of the polymer attached to the surface occurs through action of oxygen absorbed by the metal and the polymer. The appearance of oxygen-containing groups in the otherwise inert polymer should promote an increase in the extent of interaction with the metal. Adhesion in this case would also be increased by oxygen donor fillers [*7,57*].

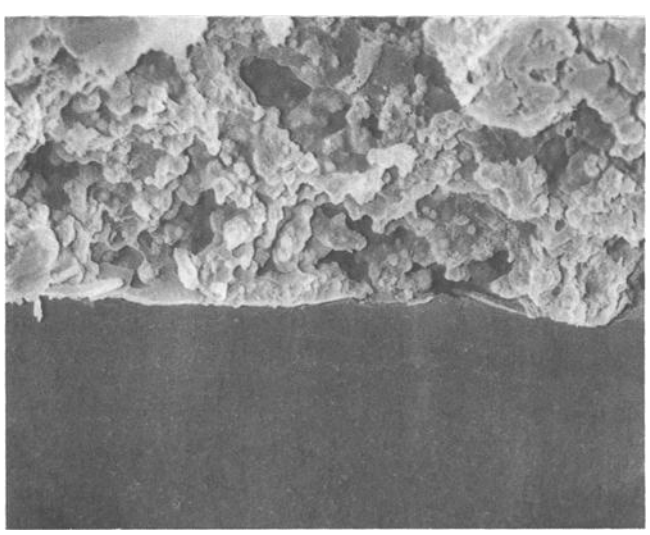


FIG. 3–SEM of sharp interface.

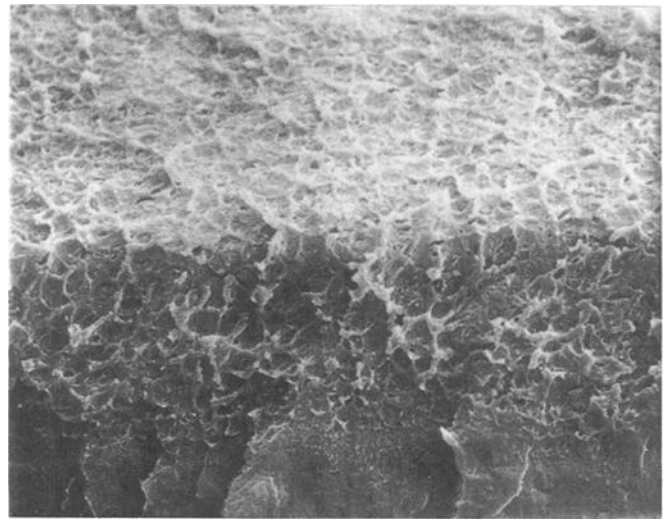


FIG. 4–SEM of diffuse interface.

All metals (except gold) are known to exist with an oxide film on their surfaces. The volume of oxide formed may be smaller than the metal reacted, and consequently the oxide film is porous and nonprotective (alkali and alkaline earth metals) or the volume may be larger and therefore protective (transition metals and aluminum). However, in the latter case, migration of metal cations from the surface leaves vacancies which aggregate to form cavities. Treatment of a metal before coating to produce a preferred or controlled bonding surface is therefore common [*7,57*]. From the above discussion, it is clear that chemical interaction between coating and solid can occur even when not recognized or anticipated.

Finally, change in substrate may impact adhesion. Weathering failures such as blistering and scab corrosion are often regarded as adhesion failures by coatings development chemists. Delamination of coatings in the absence of substrate corrosion can also be produced by weathering. A common problem involves the interfacial chalking of an epoxy primer and a topcoat that has a high UV light transmission. In the presence of UV light, moisture, and oxygen, the epoxy primer is degraded at the interface between the primer and topcoat, leading to delamination of the topcoat from the primer.

Delamination of clear or semitransparent exterior wood coatings can also occur by UV, water, and oxygen attacking the wood substrate. Delamination of the intact coating results when the wood substrate coating interface is destroyed. The solution to this problem is to add organic and inorganic UV absorbers to the coating to protect the wood substrate from degradation.

PRACTICAL ADHESION

Given the complexities of the adhesion process, can adhesion be measured? As Mittal [*3*] has pointed out, the answer is both "yes" and "no." It is reasonable to state that at the present time no test exists which can precisely assess the actual physical strength of an adhesive bond. But it can also be said that it is possible to obtain an indication of relative adhesion performance.

Practical adhesion test methods are generally of two types: *implied* and *direct*. Implied type tests include indentation or scribe techniques, rub testing, and wear testing. Criticism of these tests arises when they are used to quantify the strength of adhesive bonding. But this, in fact, is not their purpose. An implied test should be used to assess coating performance under actual service conditions. Direct measurements, on the other hand, are intended expressly to measure adhesion. Peel, lap-shear, and direct tensile are common examples. Meaningful tests of this type are highly sought after, primarily because the results are expressed by a single discreet quantity, the force required to fracture the coating/substrate bond under prescribed conditions [*2*].

Test Methods

In practice, a battery of tests is used to evaluate adhesion by inducing bond rupture by different modes. Criteria deemed essential for a test to warrant large-scale acceptance are: use of a straightforward and unambiguous procedure, relevance to its intended application, reproducibility, and quantifiability, including a meaningful rating scale for assessing performance. Test methods used for coatings on metals are: peel adhesion or "tape testing," Gardner impact flexibility testing, and adhesive joint testing including shear (lap joint) and direct tensile (butt joint) testing. These tests do not, in fact, strictly meet the criteria listed, but an appealing aspect of the above tests is that in most cases the equipment/instrumentation is readily available or can be obtained at reasonable cost [*2*].

A wide diversity of test methods has been developed over the years. In this chapter only selected test methods developed through the consensus process will be discussed in detail. The reader should recognize, however, that numerous test methods have been developed which measure aspects of adhesion [*7,58–61*] and that there generally is difficulty in relating these to basic adhesion phenomena.

The Tape Test

By far the most used test to access coating "adhesion" is the peel test. In use since the 1930s, in its simplest version, a piece of adhesive tape is pressed against the paint film. The test consists of observing whether the film is peeled off when the tape is removed. The method can be refined to measure the force required for film removal. In other tests, crosses or a cross-hatched pattern are cut into the coating, a tape applied and removed, and the coating removal assessed against an established rating scale. The currently widely used version was published in 1974 as ASTM D 3359, Standard Test Methods for Measuring Adhesion by Tape Test. Two test methods are covered.

These test methods cover procedures for assessing the adhesion of coating films to metallic substrates only by applying and removing pressure-sensitive tape over cuts made in the film. Method A is primarily intended for use at job sites, while Method B is more suitable for use in the laboratory. The cross-hatch test, Method B, is not considered suitable for films thicker than 5 mils (125 μm). Both test methods are used to establish whether or not the adhesion of a coating to a substrate is at a generally adequate level. They do not distinguish between higher levels of adhesion for which more sophisticated methods of measurement are required. In multicoat systems, adhesion failure may occur between coats so that the adhesion of the coating system to the substrate is not determined. In Test Method A an X-cut 1.5 in. (3.8 cm) long is made in the film (to the substrate) with a sharp cutting device. A 1-in. (2.5-cm)-wide pressure sensitive tape is applied over the cut and firmly adhered with a pencil eraser and then removed, and adhesion is assessed qualitatively on a 0 to 5 scale.

In Test Method B, a lattice pattern with either six or eleven cuts in each direction is made in the film (to the substrate), pressure-sensitive tape is applied over the lattice and then removed, and adhesion is evaluated by comparison with descriptions and illustrations.

For Test Method A, the following rating scale is used:

- 5A No peeling or removal.
- 4A Trace peeling or removal along incisions.
- 3A Jagged removal along incisions up to 1/16 in. (1.6 mm) on either side.
- 2A Jagged removal along most of incisions up to 1/8 in. (3.2 mm) on either side.
- 1A Removal from most of the area of the X under the tape.
- 0A Removal beyond the area of the X.

For Test Method B, 3/4 in. (1.9 cm) cross-cuts are made.

For coatings having a dry film thickness up to and including 2.0 mils (50 μm), eleven cuts are spaced 1 mm apart.

For coatings having a dry film thickness between 2 mils (50 μm) and 5 mils (125 μm), six cuts are spaced 2 mm apart.

For films thicker than 5 mils (125 μm), Method A is used instead of Method B. For Test Method B, adhesion is rated according to the following scale (as illustrated in Fig. 5.):

- 5B The edges of the cuts are completely smooth; none of the squares of the lattice is detached.
- 4B Small flakes of the coating are detached at intersections; less than 5% of the area is affected.
- 3B Small flakes of the coating are detached along edges and at intersections of cuts. The area affected is 5 to 15% of the lattice.
- 2B The coating has flaked along the edges and on parts of the squares. The area affected is 15 to 35% of the lattice.
- 1B The coating has flaked along the edges of cuts in large ribbons, and whole squares have detached. The area affected is 35 to 65% of the lattice.
- 0B Flaking and detachment worse than Grade 1.

Repeatability within one rating unit is generally observed for coatings on metals for both methods, with reproducibility of 1 to 2 units. The method is widely used and is viewed as "simple" as well as low in cost.

Peel Adhesion Testing on Plastic Substrates

ASTM D 3359 has drawn fire when used for substrates other than metal, such as plastics. The central issues are that the test lacks reproducibility and does not relate to its intended application. Both concerns are well founded. Poor reproducibility is a direct result of several factors intrinsic to the materials employed and the procedure itself. More importantly, in this instance the test is being applied beyond its

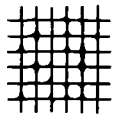
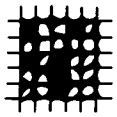
Classification	Surface of cross-cut area from which flaking has occurred. (Example for six paralled cuts)
5B	None
4B	
3B	
2B	
1B	
0B	Greater than 65%

FIG. 5–Classification of adhesion test results. From ASTM D 3359.

intended scope. ASTM D 3359 was designed for relatively ductile coatings applied to metal substrates, not for coatings (often brittle) applied to soft plastic parts [*1*].

Nevertheless, the tape test enjoys widespread popularity. The tape test is economical to perform, lends itself to job site application, and most importantly, after decades of use, people feel comfortable with it. Unfortunately, the often unique functional requirements of coatings on plastic substrates dictate that the tape test as written may not be a satisfactory measure of practical adhesion performance.

When a flexible adhesive tape is applied to a rigid coated substrate surface and then removed, the removal process has been described in terms of the "peel phenomenon," as illustrated in Fig. 6.

Peeling begins at the "toothed" leading edge (at the right) and proceeds along the coating-adhesive interface. It is reasonable to assume that any coating removal is due to a tensile force generated along this interface, which would be a function of the rheological properties of the backing and adhesive layer materials and the strength of the bond between the adhesive layer and the coating surface. Note, however, that in actuality this force is distributed over a discreet distance (0 to A on Fig. 6), which relates directly to the properties described [*63*], not concentrated at a point (0 on Fig. 6) as in the theoretical case, though tensile force is greatest at the origin for

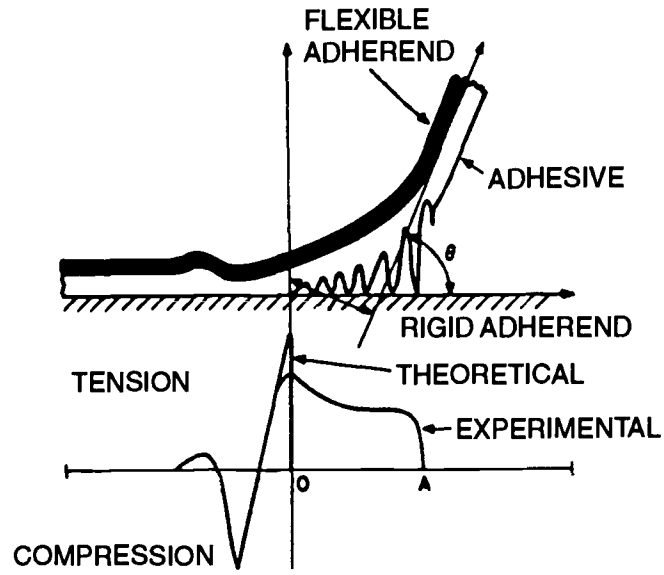


FIG. 6–Peel profile [*62*].

both. It is worthwhile to note the significant compressive force which arises from the response of the tape-backing material to being stretched, which precedes the tensile force. Both tensile and compressive forces are involved in tape testing.

Close scrutiny of the tape test with respect to the nature of the tape employed and certain aspects of the procedure itself reveal several factors, each or any combination of which can dramatically affect the results of the test as discussed below.

The Tape Controversy

Given the withdrawal of the originally specified tape, 3M-710, ASTM D 3359-91 no longer specifies a specific tape. Differences in tapes can lead to different results for reasons noted above since small changes in backing stiffness and adhesive rheology cause large changes in the tension area. It is also important to note that tapes, like most products, are manufactured to meet minimum standards. A given lot may surpass these criteria and be suitable for general market distribution, but a source of serious and unexpected error for tape testing [*63*]. There was, in fact, a commercially available tape test kit which included a tape with adhesion variations of up to 50% claimed by the manufacturer [*64*]. And, of course, tapes age on storage. Bond strengths change over time.

While there are tapes available which would appear to deliver consistent performance, a given tape does not adhere equally well to all coatings. For example, the peel removal force of the tape previously recommended by ASTM (3M-710) was examined with seven coatings. It was found that while peel was indeed consistent for a given coating, it varied by 25% between the highest and lowest ratings among coatings. This observation could be the result of several factors, notably coating composition and topology, but the bottom line is that no single tape is likely to be suitable for testing all coatings. It is also useful to note the tape test does not give an absolute value for the force required for bond rupture, but serves only as an indicator that some minimum value for bond strength was met or exceeded [*1,2*].

Procedural Problems

The tape test is operator intensive. By design it was made as simple as possible to perform and requires a minimum of specialized equipment and materials which must meet certain specifications. Therefore, the burden of accuracy and reproducibility relies largely upon the skill of the operator and his/her ability to perform the test in a consistent manner. Key steps which directly reflect the importance of operator skill include the angle and rate of tape removal and the visual assessment of the tested sample. It is not unexpected that different operators might obtain different results [*1,2*].

Peel Angle and Rate

The standard requires that the free end of the tape be removed rapidly at as close to a 180° angle as possible. But if peel angle and rate vary, the force required to remove the tape can change dramatically. Nearly linear increases were observed in peel force approaching 100% as peel angle was changed from 135 to 180°, and similar large differences can be expected in peel force as peel rate varies. These effects are related in that they both reflect certain rheological properties of the backing and adhesive which are molecular in origin, but the most useful conclusion is that these phenomena can make large contributions and must be minimized to assure reproducibility [*65*].

Visual Assessment

The final step in the test is visual assessment of coating removed from the specimen, and this can be subjective in nature. This assessment can vary among individuals evaluating the same specimen [*65*].

Performance in the tape test is based on the amount of coating removed compared to a relative scale. But it was found that the exposure of substrate can be due to factors other than coating adhesion, arising from the requirement that the coating be cut (hence the synonym "cross-hatch adhesion test"). Justification for the cutting step is reasonable; cutting provides a free edge from which peeling can begin without having to overcome the cohesive strength of the coating layer. This might be suitable for coatings applied to metal substrates, but for coatings applied to plastics, the cutting process can lead to false indications of poor adhesion. This is due to the unique interfacial zone mentioned earlier. For coatings on soft plastics, how deep should this cut penetrate? Is it possible to cut only to the interface?

If microscopic examination of panels is included, in several instances it is clearly evident that coating removal results from substrate failure at or below the interface, not from adhesive failure between coating and substrate. At the same time, it is also observed that cohesive failure within the coating layer is a frequent occurrence. The latter observation is significant in that the tape test assessment criteria make no provision for it [*1,2*].

Direct Tensile Testing

A long-used approach to coating adhesion testing is the direct tensile test, perhaps "conceptually" the simplest of all methods for measuring adhesion. A dolly or stud is bonded to the coating film. The normally applied force which is required to remove the film is measured. If failure occurs at the substrate-film interface, this force is taken to be the "force of adhesion." An obvious limitation is, of course, the strength of the adhesive bond of the stud to the cured coating. Such methods have been available since the 1930s. Many of these test methods have unfortunately suffered from their own lack of reproducibility. This is not unexpected since the forces involved are not quite as simple as appearance would have it [*5,66*].

It is essential that the force is applied strictly in the direct normal to the sample and that no bending moment is active across the test area. Deviations from symmetry in the test arrangement, poor alignment, deviations from homogeneity and of thickness of the adhesive (coating), and random variations in the strength of the bond between film and substrate affect test results [*5,66*].

The stress at locations where the adhesive film is thinner will be higher than the average stress and will be transmitted to the film under test. Another factor may be peeling during test, which is not easily identified or analyzed.

The adhesive used to bond a stud to the coating has the potential to influence the coating film properties by penetration through the film into microcracks and possibly into the substrate [*66*]. Test adhesive flexibility may also be an issue, as well as the flexibility of the substrate, if the sample is unrestrained.

There exist now within ASTM both laboratory and field versions of direct tension tests for coatings. Test Method for Measuring Adhesion of Organic Coatings to Plastic Substrates by Direct Tensile Testing, ASTM D 5179, while limited to organic coatings on plastics, uses a restrained sample and commonly available tension test apparatus. The second, Method for Pull-Off Strength of Coatings Using Portable Adhesion-Testers, ASTM D 4541, defines a class of portable pull-off adhesion testers for field evaluation of coating adhesion. ASTM D 5179 is the successor to numerous attempts to develop a reproducible coating tension test and was approved in 1991. It will be discussed first.

ASTM D 5179

This test covers the laboratory determination of adhesion of organic coatings to plastic substrates by mounting and removing an aluminum stud from the surface of a coating and measuring the force required to break the coating/substrate bond with a tensile tester. The test method provides an inexpensive test assembly which can be used with most tensile test machines. The method is used to compare the pull-off strength (commonly referred to as adhesion) of coatings to various plastic substrates, thus allowing for a quantitative comparison of various coating/substrate combinations.

A carefully prepared aluminum stud is bonded directly to a coated, cured panel using a cyanoacrylate adhesive. The adhesive is allowed to cure for 2 h at room temperature. Adhesive buildup is removed from around the stud. The specimen is then subjected to test on a tensile tester equipped with an upper coupling adapter and a restraining device (Fig. 7) to provide for sample alignment and minimal substrate flexing. The sample bearing the stud is installed in the restraining device, with only the stud pertruding. The tensile machine crosshead is lowered so the upper coupling adaptor can be attached to the specimen.

When testing thin substrates, a piece of plastic is placed in the restraining device behind the specimen to insure a rigid

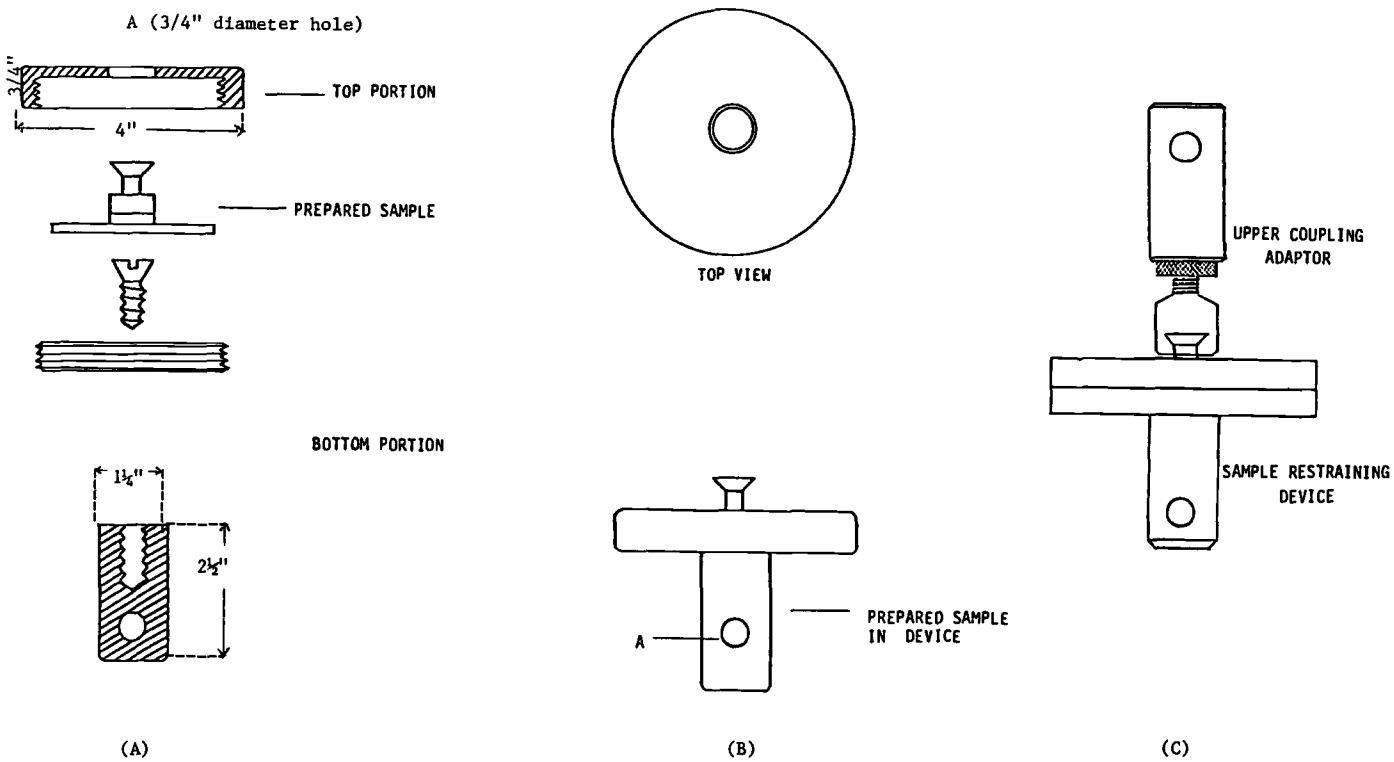


FIG. 7–Direct tensile restraining device. From ASTM D 5179.

assembly. The tension test is conducted, and pull strength recorded. Each specimen is rated according to type of coating failure, as follows:

- A Adhesive failure of the coating from the substrate.
- C Cohesive failure in the coating.
- AC Combination of adhesive failure at the coating/substrate interface and cohesive failure in the coating.
- S Adhesive failure at the stud.
- CS Combination of adhesive failure at the stud and cohesive failure in the coating.

For multilayer coatings, failure between the layers is noted and labeled as CM. Five specimens of each coated substrate are tested one day and five on a second day. If one specimen differs significantly from the other four tested at the same time, fails because of an uneven (nonplanar) stud, or for another reason performs unlike the other four, a replacement specimen is tested. The stud and specimen are carefully examined. The adhesive should have been applied uniformly to the entire stud surface. Coating should have pulled off uniformly over the *entire* stud surface either with adhesive failure from the substrate (A) or cohesive failure in the coating (C). If failure is less than 90% A or C (or CM), if the adhesive has failed at the stud, a retest, exercising particular care in the specimen and stud preparation is performed. Pull strength for the ten runs on each coating substrate combination are averaged and reported.

The precision and bias are primarily dependent upon the accuracy of the force measurements, the alignment of the device, and the care exercised in stud and specimen preparation and in the care in testing. A ten-laboratory round robin on ten samples gave an average standard deviation of 29% for reproducibility and 22% for repeatability. A range of pull strengths of two orders of magnitude has been observed (Table 1) for diverse coating-plastic combinations.

ASTM D 4541

This test method defines a class of portable adhesion testers for measuring the pull-off strength of coatings. The method covers a procedure and apparatus for evaluating pull-off strength by determining either the greatest perpendicular force (in tension) that a surface area can bear before a plug of material is detached or whether the surface remains intact at a prescribed force (pass/fail). Failure will occur along the weakest plane within the system comprised of the test fixture, adhesive, coating system, and substrate and will be exposed by the fracture surface. The method maximizes tensile stress as compared to the shear stress applied by other methods such as scratch or knife adhesion, and results are not comparable. It is recognized that the pull-off strength reflects both material and instrumental parameters and therefore provides a relative, not absolute, measure of adhesion. The pull adhesion testers defined are portable and capable of applying a concentric load and counter load to a single surface so that coatings in the field can be tested even though only one side is accessible. Measurements are limited by the strength of adhesion bonds between the loading fixture and the specimen surface or the cohesive strength of the substrate. The pull-off test is performed by securing a "loading fixture" (dolly or stud) normal (perpendicular) to the surface of the coating with an adhesive. After the adhesive is cured, the testing apparatus is attached to the loading fixture and aligned to apply tension normal to the test surface. The force applied to the loading fixture is then gradually increased (in less than 100 s) and monitored until either a plug of coating material is

TABLE 1—Representative pull strength for organic coatings on plastics.

Sample No.	Coating	Substrate	Failure Mode	Pounds Per Square Inch[a]
1	Lacquer	Polyester/polycarbonate	C	58
2	Lacquer	Polycarbonate	A	36
3	Lacquer	ABS	C	82
4	Lacquer	Polycarbonate	A	37
5	Lacquer	ABS	C	93
6	Lacquer	PVC	AC	103
7	Enamel	Polycarbonate	A	308
8	Urethane	ABS	A	639
9	Urethane	ABS	A	476
10	Urethane	Metal	S	666
11	Enamel	Metal	75% A	342
12	Lacquer	PPO/Nylon	C	226
13	Enamel	PPO/Nylon	C	226
14	Enamel	PPO/Nylon	A	242

[a]To convert to metric, multiply by 6.89 kPa.
NOTE: ABS = acrylonitule-butadiene-styrene
PVC = polyvinyl chloride
PPO = polyphenylene ether

detached or a specified value is reached. The nature of the failure is assessed as to the percent of adhesive or cohesive failure, and the actual interfaces and layers involved are identified. The pull-off strength is computed based on the maximum indicated load, the instrument calibration data, and the original surface area stressed (Fig. 8).

This method is general and is applicable to any portable apparatus meeting the standard's basic requirements for determining the pull-off strength of coatings. Four apparatus are commonly recognized to meet the requirements of the standard.

It is known that the rigidity of the substrate affects pull-off strength results and is not a controllable test variable in field measurements as defined by this standard. For example, steel substrates of less than 1/8 in. (3.2 mm) thickness show reduced pull-off strength results compared to 1/4-in. (6.4-mm)-thick panels.

Errors in measurement in this test result from alignment of the apparatus that is not normal to the surface, poor definition of the area stressed due to improper application of the adhesive, poorly defined glue lines and boundaries, holidays in the adhesive caused by voids or inclusions, improperly prepared surfaces, and sliding or twisting of the fixture during the initial adhesive cure. Also, scratched or scored samples may contain stress concentrations leading to premature fractures. Interlaboratory data have been obtained for four commercial test apparatus and are presented in Table 2.

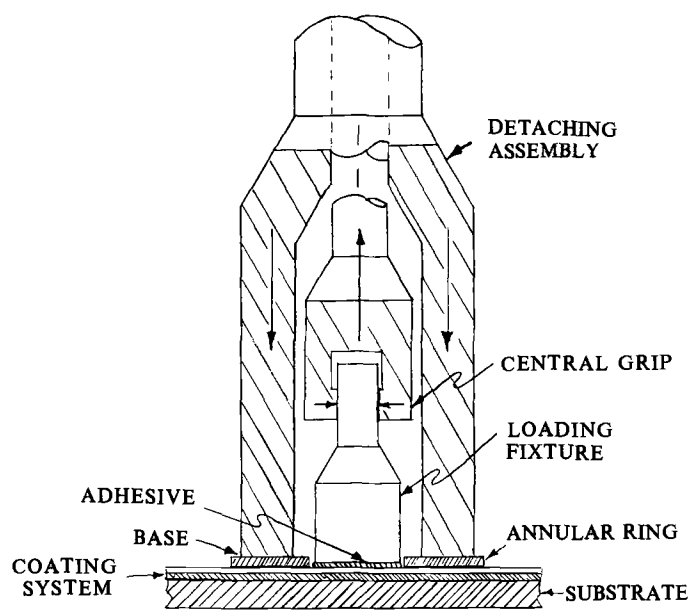


FIG. 8—Portable adhesion tester. From ASTM D 4541.

ISO 4624

Similar pull-off test methodology has been approved through the International Standards Organization, and the parameters involved have been carefully studied. ISO 4624, "Pull-off Test for Adhesion," was approved in 1978. ISO 4624 specifies two different tests assemblies (A and B of Fig. 9)

Test Assembly A (Sandwich Method) consists of a substrate painted on one or both sides, with test cylinders (studs) with a specified diameter bonded coaxially to the coated test surface and on the reverse. Test Assembly B consists of a rigid substrate coated on one side, with one test cylinder (stud) applied to that side only. While the latter is the more practical, Test Assembly A on stress analysis shows a smoother stress distribution than B. Test Assembly B shows strong stress peaks at the coating layer periphery. The result is that the Test Assembly B shows 20 to 60% lower breaking strength results than the sandwich method for several organic coatings on metal [*67*].

For Test Assembly B, breaking strength values have been shown to be a function of the diameter of test cylinders (studs) as well as their geometry. On the range of 10 to 28 mm diameters, a factor of two in breaking strength was seen with a peak at about 14-mm diameter. It was observed that tensile forces only affected the central part of the test area. Even test cylinders of the same diameter, but different shapes, gave different results, up to 45% lower. It has been noted that while uniform tensile stress can only be approached, the length of the test cylinder (stud) should be no less than half its diameter. When this is done, similar results are achieved regardless of cylinder diameter [*67*].

TABLE 2—ASTM D 4541 interlaboratory data.

Instrument	Patti	Elcometer	Hate	Dyna
Loading Fixture Diameter	13 mm	20 mm	19 mm	50 mm
Paint Sample		(mean of 3 results)		
A	1160	586	1185	201
B	1099	674	1157	185
C	1033	827	1245	190
D	1678	888	1686	297

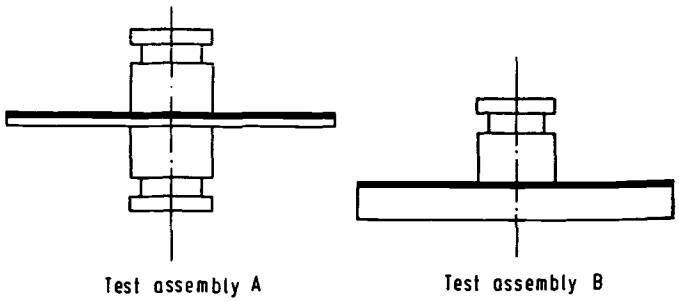


FIG. 9–ISO 4624 test assemblies.

Perhaps it is only coincidence, but it is interesting to note in Table 2 for apparatus meeting ASTM D 4541 that the loading fixture diameter and geometry differ significantly and at least partially account for the greater than a factor of 4 variation in test results, with the apparatus having a 50-mm loading fixture diameter showing the lowest numerical results.

Substrate thickness (flexibility) has a significant effect upon results. In a study of steel panels in the range of 2 to 30 mm thick, breaking strength increased to a thickness of 15 mm using Test Assembly B. A comparison of results with the sandwich method for substrates above 15 mm thickness, however, still showed breaking strength values about one third higher for Test Assembly A. These observations can be explained in terms of differences in stress distribution. Thinner substrates show increased stress intensity at the periphery, which is distinguishable up to 15-mm thickness [*67*].

ISO 4624 specifies that tensile stress shall not be increased at a rate greater than 1 MPa/s, so that failure occurs within 90 s of initial stress application. An investigation of the rate of tensile stress increase in the range 0.15 to 1.2 MPa/s yielded indistinguishable results [*67*].

Sample parameters are important. Coating thickness (and adhesive thickness) is a key factor. The energy stored in a 5-mil (125-μm) coating, by virtue of its internal strain, increases as the coating thickness increases and at a particular thickness can be sufficient to overcome the work of adhesion at the interface (spontaneous peeling). The variation is largest at thicknesses below 125 μm (5 mils), which of course is the area of most practical application. It was also observed that at the lowest coating thickness for the coatings studied, cohesive failure occurred in the uppermost parts of the coating, leaving a very thin film of coating on the test cylinder (stud). With thicker coatings, the fracture propagated deeper into the coating. Through study of the locus of failure, one can also study the effects of environmental conditions (aging, solvents, moisture) and of coating resin cure [*67*].

Clearly, stress distribution changes, as altered by test apparatus and sample parameters, can alter results dramatically. Pull-off strength (breaking strength) is therefore a relative number. Comparisons must be made carefully in concert with an examination of the locus of failure. Practically speaking, while absolute values are only approached, relative values and studies of the locus of failure are sufficient for most purposes.

ASTM D 2197

Used to a lesser extent than the preceding methods is ASTM D 2197, Test Methods for Adhesion of Organic Coatings by Scrape Adhesion.

This test method covers the determination of the adhesion of organic coatings such as paint, varnish, and lacquer when applied to smooth, flat (planar) panel surfaces. The materials under test are applied at uniform thickness to planar panels, usually sheet metal of uniform surface texture. After drying, the adhesion is determined by pushing the panels beneath a rounded stylus or loop loaded in increasing amounts until the coating is removed from the substrate surface.

The method is most useful in providing relative ratings for a series of coated panels exhibiting significant differences in adhesion. The balanced-beam, scrape-adhesion tester (Fig. 10) consists of a balanced beam to which is secured a platform for supporting weights and a rod at an angle of 45° that holds the scraping loop. The rod is set so that the scraping loop contacts test surfaces directly below the weights. The loop is a 1/16-in. (1.6-mm)-diameter rod bent into a "U" shape with an outside radius of 0.128 ± 0.002 in. (3.25 ± 0.05 mm) hardened to Rockwell HRC 56 to 58 and chromium plated and polished.

At least 1/2 in. (1.3 cm) at the end of a test panel is uncoated. The surface of the substrate must be hard enough so that it is undamaged by the scraping loop. The test procedure is as follows. A test panel on the sliding platform is placed so that it may be moved away from the operator and the uncoated portion is toward the main beam support. Weights are placed on the weight support using an initial amount estimated to be appropriate for the particular coating. The beam is lowered until the loop rests on the uncoated portion of the specimen and the full load is applied; then the sliding platform is slowly pushed away from the operator 1 to 2 s/in. for a distance of at least 3 in. (76 mm). If the coating is removed, the testing is continued using successively smaller loads (0.5-kg increments) until the coating is not removed. If the coating is not removed by the initial scrape, the testing is continued, using successively larger loads (0.5-kg increments) until the coating is removed or until the maximum load of 10 kg has been applied. A new area of the test surface is used each time a scrape is made. When the critical load has been approximately located, the test is repeated five times at each of the three loadings: above, below, and at the load determined in the first trial.

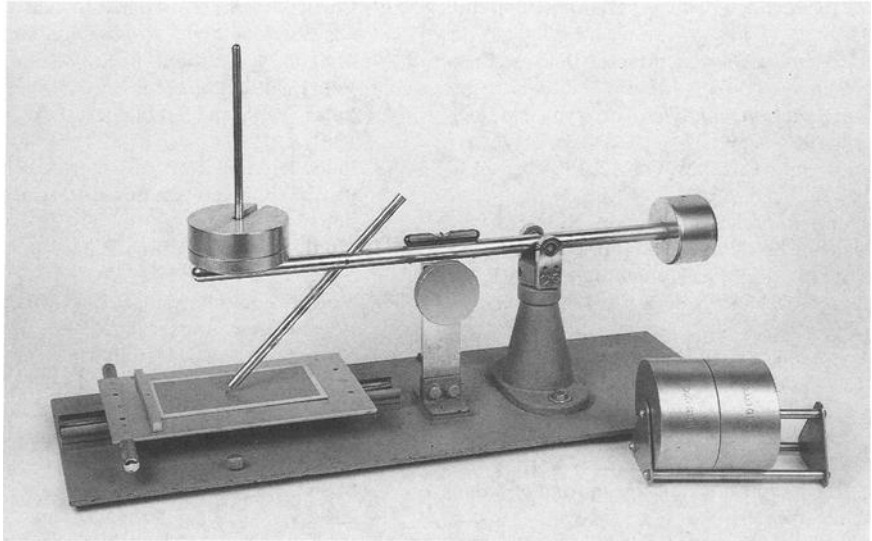


FIG. 10—Balanced-beam scrape adhesion tester.

For each applied load, the number of times the coating was removed or adhered is tabulated. The load where the scrape results change from mainly adhering to mainly removed, ignoring the first 1/2 in. (13 mm) of the scratch if the coating was removed, is the adhesion failure end point.

Other ASTM Standards

Other ASTM standards which pertain to aspects of adhesion measurements of films and coatings include the following:

ASTM B 533	Standard Test Method for Peel Strength of Metal— Electroplated Plastics.
ASTM B 571	Test Methods for Adhesion of Metallic Coatings. (This method includes bend, burnishing, chisel-knife, draw, file, grind-saw, heat-quench impact, peel, push, and scribe-grind tests).
ASTM C 313	Test Method for Adherence of Porcelain Enamel and Ceramic Coatings to Sheet Metal.
ASTM C 988	Test Method for Adherence of Porcelain Enamel Cover Coats Direct-to-Steel. (This test method is a drop weight deformation test).
ASTM D 3281	Standard Test Method for Formability of Attached Organic Coatings with Impact-Wedge Bend Apparatus. (This test method is for factory-applied organic coatings on strip metal. Adhesion loss is determined using cellulose adhesive tape.)
ASTM D 3730	Guide for Testing High-Performance Interior Architectural Wall Coatings. (This guide includes a pull-strength test for adhesion assessment).
ASTM D 4145	Test Method for Coating Flexibility of Prepainted Sheet. (This method includes a tape pull-off test).
ASTM D 4146	Test Method for Formability of Zinc-Rich Primer/Chromate Complex Coating on Steel. (This method is a tape test after dome-shaped deformation).
ASTM F 518	Practice for Determining the Effective Adhesion of Photoresist to Hard-Surface Photomask Blanks and Semiconductor Wafers During Etching.
ASTM F 692	Method for Measuring Adhesion Strength of Solderable Films to Substrates.

Additional tests exist for electrodeposits, and bending, burnishing, and wrapping tests for coatings on wire. Tests for adhesives have also been applied to coatings as well. Use of reverse impact tests, lap and butt joint tests, and tensile shear tests have been reported [*1*].

CONCLUSIONS

Basic adhesion is the summation of multiple phenomena. Ideal adhesion is probably neither obtainable nor measurable experimentally. Practical techniques do, however, allow sufficient assessment of relative adhesion for most purposes, if used with care and knowledge. Workers need to understand both basic adhesion concepts and the factors affecting practical adhesion for systems of their interest if they are to make improvements in real world products.

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Abrasion Resistance*

by Mark P. Morse[1]

THE PROBLEM OF RESISTANCE TO ABRASION exists all around us: on floors, walls, furniture, automobiles, farm implements, construction equipment, military gear, appliances, shoe soles, and so on. Because resistance to abrasion is a basic factor in the durability of a coating, its measurement is of practical importance to both producer and consumer.

Abrasion is caused by mechanical actions such as rubbing, scraping, or erosion from wind and water. It can take two general forms: marring or wearing.

DEFINITIONS

Mar abrasion consists of permanent deformations that have not ruptured the surface of a coating. The resistance of a coating to marring is its ability to withstand scuffing actions that tend to disfigure or change the appearance of its surface. Some examples of potential causes of marring of organic coatings are: (a) sliding an object across the surface of furniture; (b) rubbing of a belt buckle, button, zipper, or rough fabric on an automobile finish; (c) sliding a toy across a wall or a refrigerator door, etc.

Wear abrasion is caused by mechanical action that removes material from the surface of a coating. In many cases, the removal is gradual or progressive due to repetitive mechanical action.

RELATIONSHIP TO OTHER PHYSICAL PROPERTIES

Abrasion resistance is not a unique or isolated property of a material but is rather related to other physical characteristics such as hardness, cohesive and tensile strength, elasticity, and toughness. Also, from the standpoint of retaining its protective or decorative function, the thickness of a coating can be an important factor.

Hardness, Elasticity, and Tensile Strength

Abrasion resistance is related to hardness, yet the relationship is not simple. A first thought might be that the harder a coating, the better would be the abrasion resistance; however, this is not always true. Steel is much harder than rubber, for example, but steel "tires" on an automobile, in addition to not giving a smooth ride, would not last long on concrete roads in comparison to the service life of a good rubber tire. The ability of a material, such as a rubber tire, to undergo elastic deformation and recover or "to ride with the blow" is associated with good abrasion resistance.

The energy transferred to an elastic material by an impacting object is largely returned to the object, though redirected, instead of being expended in the destruction (separation and removal of material) of the impacted surface. From a fundamental viewpoint, this is a consequence of the smaller deceleration and hence smaller force generated, since force is equal to the product of mass and acceleration, when the impact is with a material that will deform or "give" with the impacting object. If the deformation caused by the object is not elastic, the material will yield and flow, causing damage. Therefore, soft materials with a low tensile strength are not abrasion resistant.

The fact that elastic materials are often abrasion resistant does not mean that hard materials are not abrasion resistant. Theoretically, however, if one is given two materials of equal tensile strength, the material of lower modulus should have the best abrasion resistance. The deceptive factor here is that a hard material usually has a much higher tensile strength than a soft material. Thus, when a rubber is compared with steel, materials with orders of magnitude difference in tensile strength are being considered. The fact that rubber is abrasion resistant emphasizes that the value of a low modulus of elasticity and adequate tensile strength are factors that play a role in obtaining good abrasion resistance.

In theory, a very hard material that has a hardness and cohesive strength adequate to completely resist any impact force it might encounter would not be dependent on rubber-like elasticity to reduce or dissipate impact stresses. It would be more abrasion resistant than the best elastic but weaker material [*1*].

CORRELATION WITH END-USE PERFORMANCE

From the discussion above, it is apparent that the measurement of abrasion resistance involves measuring a complex combination of interrelated properties among which there is no direct relationship. The task of devising a test methodology that will correlate with end-use performance is, therefore, complex and difficult but not impossible to develop. If the test method subjects the material under test to a composite of destructive forces similar to those met in service, then

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[1]Consultant, 71 S. Shelburne Road, Springfield, PA 19064.

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the test method will correlate—or predict—the service performance of the material in at least a qualitative or relative ranking respect.

When accelerated tests are being considered, even tests that rank materials in the same sequence as actual service tests, a quantitative correspondence with actual service is seldom expected or obtained. Actual end-use tests, while the most reliable in providing an indication of a material's probable long-term durability, suffer from the difficulties of ensuring equivalent usage and measurement, especially when the comparison of different materials is attempted. Because of such difficulties and because service tests are usually very time consuming, a wide variety of test machines have been developed to provide an accelerated indication of the abrasion resistance of coatings and related materials such as vinyl flooring, linoleum, and wall coverings. In a comprehensive review article by Harper [*2*], there is a list of no less than 49 different abrasion-causing machines. An investigation by the International Study Committee for Wear Tests of Flooring Performance [*3*], in which seven commercial, organic flooring materials were systematically tested on 21 abrasion machines of 17 different types, indicated that very few of these machines were capable of providing a reliable comparison of the abrasion resistance of widely different materials that could be correlated with end-use performance. In addition, the different machines did not correlate very well with each other.

On the basis of a round robin conducted in 1956 by ASTM with six different clear floor coatings evaluated by six different abrasion test methods [*4*], only two of the methods were found to correlate with actual end-use performance and to have the reproducibility necessary for acceptance as ASTM standards. These were ASTM Test Method for Abrasion Resistance of Organic Coatings by Falling Abrasive (ASTM D 968) and ASTM Test Method for Abrasion Resistance of Organic Coatings by Air Blast Abrasive (ASTM D 658). The jet abrader, Method 6193 of Federal Test Method Standard No. 141C, which became available after the testing, appears to correlate well with the two cited ASTM methods and with various types of end-use performance. In addition, the jet abrader offers greater speed and precision of measurement [*1*]. Even today, with other tests also available, these tests are still important and widely used. However, more recent comparative testing (see **COMPARISON OF WEAR ABRASION TESTERS**) indicates ASTM D 658 is superior to ASTM D 968 and that ASTM Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser (ASTM D 4060) is superior to both of these tests as regards precision and sensitivity in differentiating between coatings.

MECHANISM OF ABRASION

The success of the particle impingement types of abrasion testers in correlating with service performance is perhaps not surprising when one considers the abrading mechanism. Whether or not a particular type of abrasion test correlates with end-use performance depends not only on a similarity of abrading mechanisms in both cases, but also on the extent to which that mechanism is maintained during the course of the abrasion test. It is on the latter factor that many methods fail.

Rubbing (friction) and scraping methods obviously wear away the test surface in a different manner than methods in which abrasive particles are contacted with the surface. One aspect of the mechanistic difference lies in the angle of contact with the surface. Abrasive particles striking the surface of a coating at nearly normal incidence tend to compress, scar, and cut into the coating. As a result, minute portions of the coating eventually should be crosscut and displaced. On the other hand, the rubbing and scraping types of abrasion that take place at near grazing incidence would tend to undercut and to shear through very thin layers of the coating in successive, irregular slices that ultimately wear it away. Different devices might incorporate various degrees of these basic processes, depending on the angle and force of particle attack.

Apart from the nature of the above mechanisms, it should be apparent that whatever the mechanism, it is not maintained uniformly in friction methods. Such methods suffer from changes in the abrading conditions as the testing proceeds, either because of heating of the specimen or clogging of the abradant or other.

If an abrasion test using the direct impingement of particles is chosen so the undesirable frictional effects are avoided, there may be doubt about whether the method correlates well with a type of service in which the coating is, for example, walked upon. Yet, the previously mentioned ASTM round robin of abrasion tests carried out with floor coatings clearly established the validity of particle-impingement-type tests for evaluating this type of end-use service life.

Until the mechanism of abrasion is more completely studied and understood, industry must continue to rely to a large extent on experimentation and even intuition when devising abrasion test methods. In addition, properly designed test programs must be employed to determine the extent to which a given method correlates with actual end-use performance [*1*]. A side variety of useful abrasion testing procedures are described in sections that follow.

LOOSE FOR FALLING ABRASIVE METHODS

Falling Abrasive Test

This widely used abrasion test method has both ASTM and federal counterparts. Originally developed at Gardner Laboratory [*5*], the method has been studied and further developed by others [*6*]. ASTM D 968 employs an apparatus, Fig. 1, that is simple and inexpensive compared with other more complicated instruments, and the test results correlate reasonably well with various types of service [*4*]. However, the method is laborious and time consuming since large quantities of abrasive must be handled due to the slow rate of abrasion, particularly when the material under test is abrasion resistant.

Over the years a variety of abrasives have been used in the basic apparatus. These abrasives include sand, emery, and various grades of silicon carbide (Carborundum). Sand, although having the disadvantage of a slow abrasion rate, is readily available and has given reproducible results at low cost. Therefore, it has been the abrasive of choice in the standard methods. Only sand and silicon carbide are used in

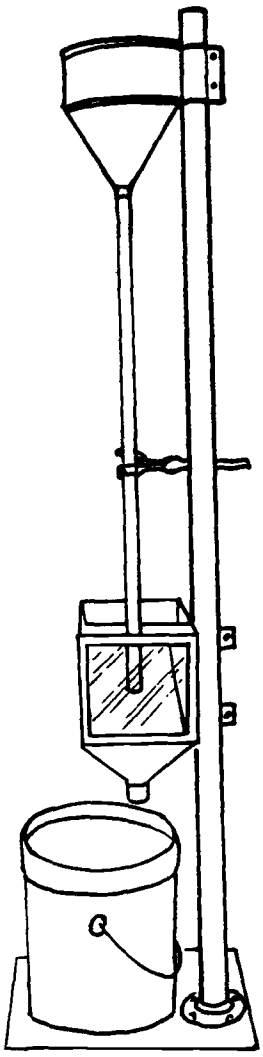

FIG. 1—Falling sand abraser (courtesy of Paul N. Gardner Co.).

ASTM D 968, which specifies that a natural silica sand graded to a particular sieve size and known as Ottawa sand is the standard sand abrasive and a silicon carbide of particular sieve size is the other standard abrasive. Abrasion resistance is expressed in terms of the volume of abrasive required to wear through a unit thickness of the coating with the abrasive falling from a specified height through a guide tube. The substrate is supported at a 45° angle to the vertical.

Pebble Abrasion Wear Test

This test method was originally developed as an adhesion test for floor finishes, but it is more properly classified as an abrasion test. The coatings to be investigated are applied to the walls of a hexagonal iron box; 6 lb (2.72 kg) of flint pebbles are placed in the box, and then the box is rotated so that the pebbles strike the coatings. A rotational speed of 38 rpm applied for 2 h (1 h in each direction) is sufficient to differentiate most floor coatings. The apparatus for this test is not commercially available.

Gloss Reduction Test

Some methods of gloss reduction utilize the impingement of a definite quantity of abrasive coupled with measurement of gloss. A modified version of ASTM D 986 was used by Sward [*5*] to measure the effect of abrasion on paints, varnishes, and lacquers. A large guide tube of 2.5-in. (6.35 cm) diameter was used to make an abraded area large enough for gloss determinations. Ottawa sand of 20 to 30 mesh was used as the abrasive. To distribute the sand uniformly throughout the cross section of the guide tube, a wire spider web was inserted just below the outlet tube in the stream of falling sand.

ABRASIVE BLAST METHODS

Air Blast Abrasive (Bell Laboratory Abrasiometer)

ASTM D 658 employs a particular size of silicon carbide abrasive that passes from a hopper through a guide tube and impinges onto the specimen. The abrasive flow is facilitated with an air blast [*7*]. The abrasion rate is markedly greater than that obtainable with a free-falling abrasive as is used in ASTM D 968. This device, which was originally known as the Bell Laboratory abrasiometer, was adopted for use in ASTM D 658 after the good results obtained in the round robin test described under **CORRELATION WITH END-USE PERFORMANCE.** The test requires rather cumbersome test equipment and the need to replace the abrasive after it has been used five times. In addition, the abrasive must be sieved after each use to remove any large particles of coating that may have chipped off during the test. This testing device is not commercially available; however, details for its construction are available at ASTM Headquarters in Philadelphia.

A view of that part of the abrasive blast device which contains the abrasive guide tube, nozzle, and specimen stage is presented in Fig. 2. The controlled air that enters the nozzle has passed through an array of regulating devices: filters, pressure reduction valve, mercury pressure leg, air equalizing chamber, flow meter, and manometer. When it is adjusted to a standard air pressure, air flow, and abrasive flow, the device is capable of good precision.

The specimen is mounted at a 45° angle to the nozzle, which is lowered to touch the test surface. Then the air flow is adjusted to the specified pressure, and the stream of abrasive is released and allowed to flow until the coating is worn through to the substrate. The end point is considered to be reached when a worn spot about 2 mm in diameter appears in the center of the wear pattern. The abrasion resistance (abrasion coefficient) is calculated as the weight in grams of abrasive required per mil of coating.

A device similar to the Bell Laboratory abrasiometer was designed by Koch at Hercules [*8*]. The main difference between the two devices is in nozzle design.

Roberts Jet Abrader

With this abrader, which is pictured in Fig. 3 and available from Kamaras Instruments, Garrett Park, MD, abrasion resistance is evaluated in terms of the time required for a closely controlled jet of fine abrasive to penetrate through the

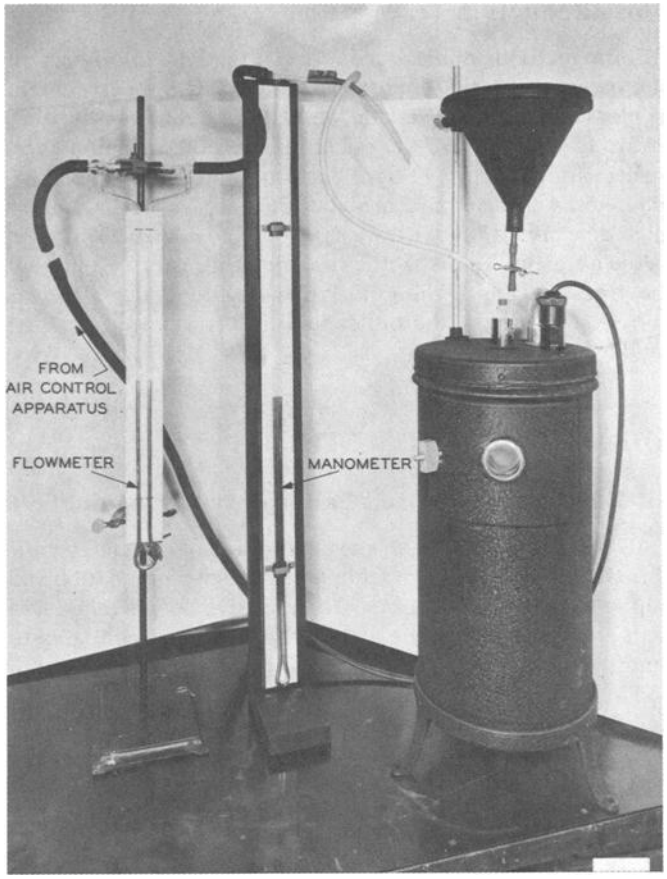

FIG. 2–Abrasion test apparatus (ASTM D 658).

FIG. 3–Roberts Jet abrader (courtesy of Kameras Instruments).

coating to the substrate. The first disclosure of bare substrate is taken as the end point, and it is visually signalled by an abrupt change in gloss or color. The high speed of the abrasive jet particles used in this test results in a rapid abrasion rate that permits most coatings to be tested in a matter of seconds.

The jet abrader method avoids the adverse heating, gumming, and abradant-clogging effects associated with the rubbing and friction methods. The small scale of operation permits the economical use of continuously fresh abrasive, and it allows a large number of tests to be made on a single 15.2 by 7.6-cm specimen. This method makes practical the use of a reference panel for instrument calibration and affords the opportunity for interlaboratory standardization of instruments and results.

A prototype jet abrader was developed at the National Bureau of Standards (NIST) [*9,10*]. The abrading conditions are set from outside the test chamber, and the abrasive flow is controlled by adjusting the voltage to the vibrator on which the abrasive storage chamber is mounted. The amplitude of vibration determines the amount of abrasive that sifts into the gas (carbon dioxide) stream.

Abrasion resistance is usually expressed in terms of time per unit thickness (seconds/mil), but coatings of the same thickness may be compared on the basis of total abrasion time. Abrasion time is proportional to coatings thickness up to about 6 mils. At greater thickness, the abrasion rate begins to decrease due to hindrance of abrasive particles in the abraded pit. Very thick coatings on the order of 100 mils may be evaluated as small specimens on which weight loss for a given abrading time is determined. This test procedure is detailed in Method 6193 of Federal Test Method Standard No. 141C. Any panel of uniform coating thickness can serve as a reference panel if it has a convenient abrasion time. A suitable reference panel can be made by bonding plastic film of uniform thickness to a rigid substrate by means of a very thin coat of adhesive.

Gravel Projecting Machine

This machine, which is commonly termed a gravelometer, is a device designed to evaluate the resistance of automotive and railway finishes to abrasion by flying gravel and road ballast. ASTM Test Method for Chip Resistance of Coatings (ASTM D 3170) has a description of such a device and provides a procedure for its use. Figure 4 illustrates the interior components of a device that meets specification given in ASTM D 3170. A test chamber is provided in which a coated panel is supported vertically and blasted with a stream of particular gravel. One pint of this gravel is introduced into an air stream having a pressure of 70 ± 2 psi (4.92 ± 0.14 kg/cm^2) over a 10-s period. Tests are usually conducted in a cold room to simulate winter-like driving conditions. At the completion of the test, the coated panel is visually rated for degree of chipping by using a photographic reference standard provided with D 3170. SAE Method J400 describes the test procedure used for evaluating the chip resistance of automotive coatings.

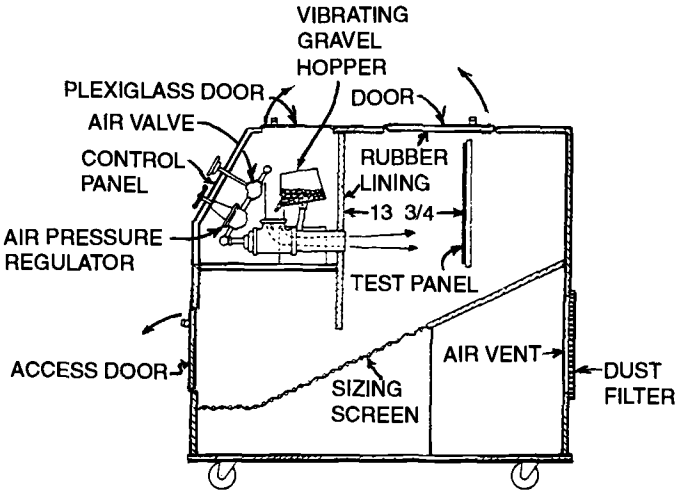

FIG. 4–Interior of a gravelometer (courtesy of the Q-Panel Company).

METHODS USING ROTATING DISKS

Bell Laboratory Rotating Disk Abrasion Test

In this method, a circular panel coated with the finish is rotated while submerged [*11*] in a bed of sand. The apparatus is illustrated in Fig. 5. A turntable to which the 4-in. (10.2 cm)-diameter specimen is mounted is contained within the hopper. Ottawa sand of 20 to 30 mesh is added to the hopper until the specimen is covered to a depth of 5 in. (12.7 cm). The disk is then rotated at speeds of 750 to 1000 rpm for several thousand revolutions as specified. During the test, the sand is circulated through a device that cleans and cools it. The amount of film material lost during a test is a measure of abrasion resistance. It is expressed as a "wear factor" that is the product of the radius of film remaining on the disk and the number of revolutions in thousands.

FIG. 5–Bell Laboratory rotating disk abrasion tester. Specimen rotates while buried in sand. (Courtesy of Bell Telephone Laboratories.)

Wolf Abrasion Method

This early method [*12*] was the forerunner of other more elaborate instruments such as the Camp and the Taber devices. A leather disk on the end of a rod is moved in a circular manner on the film being tested. The abrasion factor is given as the loss in grams per 100 cm^2 of surface.

Camp Abrasion Tester

For this test, the coating is applied to a 10.2 by 10.2-cm metal panel, and the panel is fastened to a horizontal turntable that rotates at a speed of 30 rpm beneath a weighted, circular, rubber, ink eraser (Eberhard-Faber No. 1071) that acts as the abrader [*13*]. The eraser abrader is attached to a side arm on a lever at an offset angle that causes a 0.64-cm-wide path to be worn in the film. A counter records the number of revolutions required to wear through the film. The machine is made automatic by placing a copper trailer behind the abrading disk. This trailer activates a circuit-breaking relay when it contacts the metal panel exposed by wearing away of the film. Tests can be checked within 500 revolutions in a total of 5000 to 8000 revolutions. Most coatings fail within the range of 2000 to 46 000 revolutions. The eraser abrading disks are changed after each 5000 revolutions.

FDC Wear Test

This test was devised to determine the resistance of cellulose nitrate furniture lacquers to abrasion [*14*]. It measures the loss of weight when the lacquer film is abraded by nylon fabric. The machine used, which is shown in Fig. 6, is the modified carpet abrasion machine of the Wool Industries Research Association of England. A 10.2 by 10.2-cm lacquered glass panel is attached to the plate carrier, with lacquered side down. During the test, it rotates at 37 rpm while in contact with the nylon-covered abrading head, which is also rotating at the same speed and in the same direction. However, the centers of the plate and the head are offset, which results in uniform abrasion of the film. After a specified number of revolutions and conditioning, the weight loss is determined and is taken as the abrasion resistance of the specimen.

Schiefer Abrasion Testing Machine

(This machine is available from Frazier Precision Instruments Co., Inc., 925 Sweeney Dr., Hagerstown, MD 21940.) The machine was designed for measuring wear resistance of textiles such as rugs and fabrics [*15–18*], but it offers a potentially useful means for evaluating the wear abrasion of organic coatings. It has two unique features: (a) a uniform abrasion pattern and (b) interchangeable steel and Carboloy abradent disks with crosscut and rod patterns that reduce heating and clogging (Fig. 7).

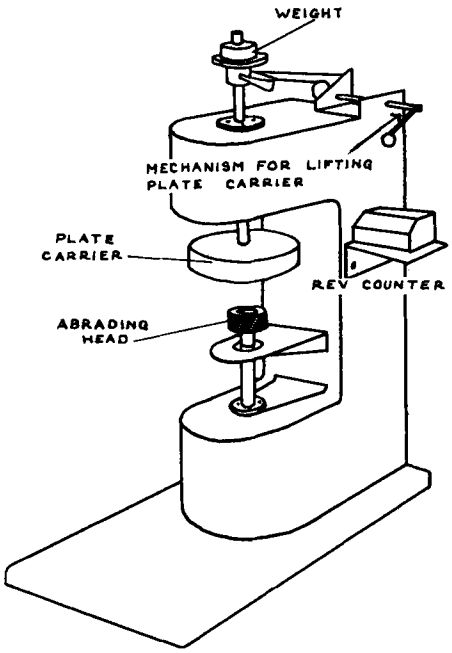

FIG. 6–FDC wear tester. Nylon fabric on rotating head is used to abrade furniture lacquer rotating on offset axis (courtesy of Furniture Development Council, England).

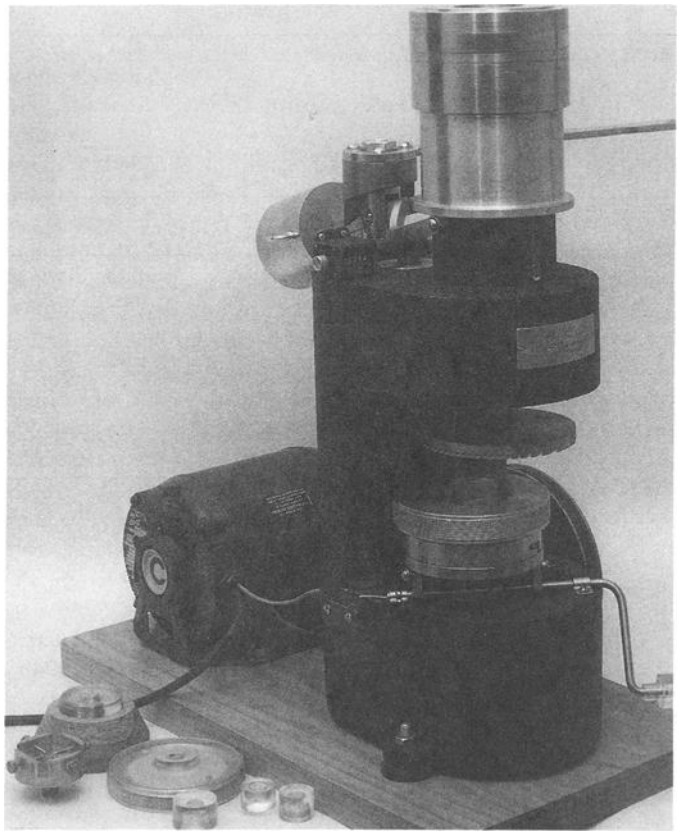

FIG. 7–Schiefer abrasion testing machine (courtesy of Frazier Precision Instrument Company).

To conduct a wear abrasion test, the specimen is mounted on a motor-driven rotating plate where it is abraded uniformly in all directions by the motion of the offset rotating abradent mounted directly above it. Both specimen and abradent rotate in the same direction with approximately the same angular velocity, 250 rpm, each about its own axis. The axes are spaced 1 in. (2.54 cm) apart and are parallel. The abradent is loaded with a standard weight.

METHODS USING ROTATING WHEELS

Taber Abraser

This apparatus, Fig. 8, is widely used for evaluating the wear abrasion resistance of organic coatings. A procedure for its use is given in ASTM Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser (ASTM D 4060), in Method 6192 of Federal Test Method Standard No. 141C, and in ISO/DIN Methods 3494 and 4584. ASTM D 4060 utilizes a specimen in the form of a 4-in. (10.2-cm)-diameter disk or a 4-in. (10.2-cm) square mounted on a turntable that is rotated at a fixed speed under a weighted abrading wheel. "Calibrase" resilient abrading wheels are designated CS-10 and CS-17 with the latter being the most abrasive. Because of the slow hardening of the rubber bonding materials in this type wheel, a wheel should not be used if it has aged longer than one year. Before each test and after every 500 cycles (revolutions), the abrading wheel is resurfaced with an abrasive disk that is placed on the turntable. A vacuum pickup is used to remove any loose particles generated during actual tests. Wear abrasion resistance is expressed in terms of (a) Wear Index, which is the weight loss per specified number of revolutions (usually 1000) under a specified load (500 or 1000 g), and/or (b) wear cycles per mil, which is the number of cycles required to wear through a 1-mil thickness of coating and is reported as the number of revolutions per mil. In an ASTM round robin, Taber abraser tests with a series of organic coatings produced abrasion resistance values that exhibited a within-laboratory coefficient of variation of 10% and an interlaboratory coeffi-

FIG. 8–Taber Abraser (courtesy of Taber Industries).

cient of variation of 30%. Another study of the reliability of test results was conducted by Hill and Nick in 1966 [*19*].

TESTS BASED ON RECTILINEAR MOTION

Straight-Line Reciprocating Machines

These machines, as shown in Fig. 9, pull a sled or boat back and forth over the surface of a coated panel. The sled surface can be a brush, a sponge, rubber, or sandpaper. A sled travel of at least 10 in. (25.4 cm) is provided by the machines, and they can provide reciprocating cycles ranging from 35 to 60 per minute.

Both dry and wet surface tests may be performed with these machines. For dry surface tests, wear abrasion resistance is reported as: (a) number of cycles to reach a certain visual end point, (b) degree of abrasion observed after a specified number of cycles, and (c) number of cycles required to abrade through the coating to the substrate.

Procedures for conducting wet adhesion (scrub resistance) tests on interior paints are described in ASTM Test Method for Wet Abrasion Resistance of Interior Paints (ASTM D 4213) and in Method 6141 of Federal Test Method Standard 141C. In these test procedures, coating films are applied to a plastic substrate and allowed to dry. A sponge surface is mounted on the sled. Both the sled and the coating surface are wet with a soap solution of specified composition. Wet abrasion resistance is reported as: (a) computed rate of erosion of the wet coating film and (b) number of cycles required to wear through the coating film to the substrate or to produce breaks in the film.

RCA Tape Tester

This device is available from Norman Tool and Stamping Co., 15415 Old State Rd., Evansville, IN 47711. It is being actively used for evaluating the abrasion resistance of appliance finishes and of coatings on television set controls. It is reported to have greater sensitivity than the Taber Abraser in determining differences in the abrasion resistance of coatings. The machine abrades a 2 by 2-in. (5.1 by 5.1 cm) coated panel surface by passing computer or polyester tape over the surface. A fresh tape surface is presented for each cycle of abrasion. Weights ranging from 55 to 275 g are applied to the tape depending on the nature of the coating under test. Abrasion resistance is reported either as the number of cycles required to produce the onset of visible scuffing or as the number of cycles required to wear through to the substrate.

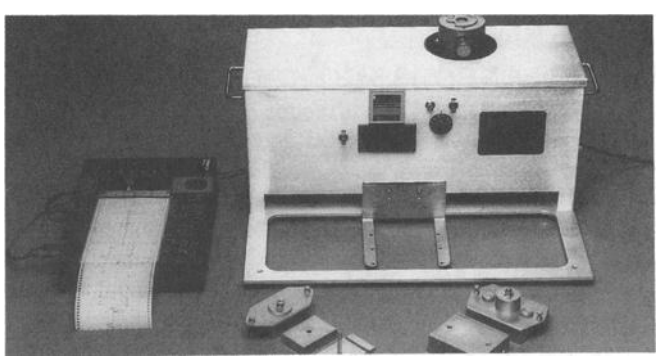

FIG. 9—Reciprocating abrasion tester. WA-2168 Model D12VFI machine with cut-out base, recorder, and several test accessories in foreground. (Courtesy of Paul N. Gardner Co.)

COMPARISON OF WEAR ABRASION TESTERS

ASTM Subcommittee D-01.23 conducted a round robin to determine the comparative precision, sensitivity, and correlation of four wear abrasion testing procedures. The procedures were (a) air blast silicon carbide (ASTM D 658), (b) falling sand (ASTM D 968), (c) falling silicon carbide (ASTM D 968), and (d) Taber Abraser (ASTM D 4060). The wear abrasion resistance of four coatings with significantly different apparent resistances to abrasion were tested with each device. The results obtained from these tests are recorded in ASTM Report RR D01-1037, which is available at ASTM Headquarters.

From the results, it was concluded that the air blast silicon carbide test and the cycles per mil Taber abraser test had better sensitivity in differentiating coating abrasion resistances than the other test procedures. The falling sand test, air blast silicon carbide test, and Taber abraser cycles per mil test ranked the coatings in the same order as the expected performance. The falling silicon carbide test reversed the ranking of two of the coatings. The precision exhibited by the four test procedures are as given in Table 1.

TEST FOR MAR ABRASION RESISTANCE

(See also above-described Gloss Reduction test.)

Balanced Beam Tester

A useful test for determination of mar resistance involves the use of a balanced beam scrape tester. ASTM Committee D-01.23 has developed a proposed test procedure using such a tester, which consists of a balanced beam equipped with a loop stylus attached to the end of a rod set at an angle of 45°. The test is carried out by placing a coated test panel on a movable platform and a weight on the beam. The stylus is lowered gently onto the coated surface, and then the platform is pushed against the stylus at a rate of ¼-in. (6 mm) per second for a distance of at least 3 in. (75 mm). At the end of each stroke the stylus is raised off the coated panel and the

TABLE 1—Comparison of abrasion resistance test method precision.

	Coefficients of Variation	
	Within Laboratory	Between Laboratories
Taber Abraser (ASTM D 4060)	4%	16%
Air Blast Silicon Carbide (ASTM D 658)	7%	10%
Falling Sand (ASTM D 968)	9%	35%
Falling Silicon Carbide (ASTM D 968)	11%	45%

panel is moved slightly to the side to provide a new test surface. The coating is examined for marring. If none is visually observed in the initial scrape, successively greater weights are added to the beam until marring is apparent. If marring is produced in the initial scrape, testing is continued using successively lighter weights until the coating is not marred. The weight required to just produce visible marring is taken as the mar resistance value. Details about the balanced beam tester and its operation can be found in ASTM D 2197, Test Methods for Adhesion of Organic Coatings by Scrape Adhesion, ASTM D 2248, Practice for Detergent Resistance of Organic Finishes, and MIL-P-7788A.

Princeton Scratch Tester

This apparatus is similar to the balanced beam tester, but instead of having a moveable specimen table, the beam assembly itself moves on a V-shaped track with the coated panel remaining immobile. The stylus is held at a 90° angle.

Impinging Abrasive Method

An impinging abrasive method is described in ASTM Test Method for Mar Resistance of Plastics (ASTM D 673) and in Method 1093 of Federal Test Method Standard No. 406. Although this test was designed for determining the mar resistance of plastics, it has a potential for determining this property of organic coatings.

The test consists of allowing a stream of silicon carbide to fall on the specimen and then determining the degree of marring by gloss measurements. The apparatus consists of a hopper that dispenses the abrasive through small openings as it rotates at 7 rpm. Abrasive flow is about 225 g per minute.

Taber Abraser Mar Test

The Taber Abraser can be used to evaluate the mar resistance of organic coatings. A mild abrading is produced by using wheels covered with paper. Mar resistance is reported as the number of cycles of rotation required to just produce a barely visible scuffing or loss of gloss.

Coin Mar Test

This test consists of dragging the edge of a coin across the surface of a coated panel and visually determining the degree of marring produced. The procedure can be used as a "pass/fail" test or for comparing the mar resistance of coatings on a relative basis. Results will vary from laboratory to laboratory due to the particular coin used and the pressure used for contact.

Fingernail Test

In this test, the back of a fingernail is dragged across the surface of a coating and the degree of marring is visually observed. The procedure can be used as a "pass/fail" test or for comparing the mar resistance of coatings on a relative basis.

RAIN OR WATER EROSION

Rain erosion resistance of aircraft coatings has been studied in two types of testing machines [*20*]—whirling arm and jet. In the whirling arm tester, specimens having an airfoil contour are fastened to the leading edges of the two arms of a propeller-like blade that is rotated at angular velocities equivalent to flying speeds of up to 700 mph. Simultaneously drops of water fall on the whirling arms. Both the simulated air speed and the quantity of "rainfall" can be varied and closely controlled. In the jet-type tester, a high-pressure jet of water impinges on the specimen. A rotating slotted disk in the path of the water jet breaks the stream of water into individual drops to simulate rainfall.

In both of the above methods, having the water in the form of individual drops is a basic principle of the test. This is because the erosion that occurs on the leading edges of the airfoils on high-speed aircraft flying through rain is often the result of cavitation produced by the high-energy impacts of a multitude of individual droplets. At very high velocities, the water droplets, in effect, behave as tiny solid projectiles.

TRAFFIC PAINT TESTS

The Dorry tester uses a crushed quartz abrasive that is fed onto a grinding plate against which the coating, face down on its paper base and weighted with 100 g of sand, is abraded.

The Hickson tester is a heavy duty, permanently mounted machine in which a motor-driven solid rubber tire is rotated against a braked rotating concrete disk on which the test paint has been applied. The test correlates quite well with the service performance of traffic paints.

The New Jersey Zinc Company (presently Zinc Corporation of America) tester is a portable machine in which a pair of rubber-tired wheels revolve in a layer of sand on the test platform.

Another tester, the abradometer, is a large machine that utilizes a motor-driven wheel set at a slight shear angle to a large wheel on the rim of which up to 46 specimens are mounted. A brake load is applied during the test.

In the Payne abrasion machine, five specimens at a time oscillate through a 25-mm distance while being abraded with an abrasive wheel.

MISCELLANEOUS METHODS

Brief mention is made to several less-well known tests that may be of interest. In The Sproul-Evans apparatus [*21*] the specimen is rotated in a cylinder containing silicon carbide powder. A procedure by Wellinger [*22*] involves using a rod coated with the test paint and rotated in a container of sand. A sensitive method for measuring the tread wear of automobile tires involving the use of a nonhazardous radioisotope of iodine was developed by Outbridge [*23*]. Conceivably, this technique could be used to evaluate the abrasion resistance of coatings. Marks and Conrad [*24*] developed an abrasion comparator apparatus that utilizes high-velocity emery particles

FIG. 10—PEI abrasion tester. Specimen in chamber on gyrating table is abraded by glass or stainless steel sphere in a slurry of abrasive particles. (Courtesy of National Bureau of Standards.)

propelled by high-pressure air to evaluate the resistance of plastics—particularly aircraft glazing—to abrasive particles. Haze due to abrasion is measured with aid of a light integrating sphere.

Although the PEI abrasion tester was designed and developed by the Porcelain Enamel Institute to measure the abrasion resistance of porcelain enamels, this tester has also proven to be useful in determining the wet abrasion resistance of organic coatings. It is specified to be used in ASTM C 448, Test Methods for Abrasion Resistance of Porcelain Enamels. The tester, which is pictured in Fig. 10, has a gyrating table with positions for nine specimens. Abrasive-retaining rings and lids are clamped over the specimen to form individual test chambers. Each chamber is charged with glass or stainless steel spheres, and a slurry of abrasive particles is added through a filling aperture located in the lid. The table gyrates at 300 cycles per minute to cause abrasion of the specimens. The amount of abrasion is evaluated by measuring the loss of gloss or loss of weight in the specimens after a specified time period.

The Peters abrasion block is based on a block that has a weight of 2 kg and a size and contour suited to hand operation. Three 50 by 80-mm abrasive surfaces are provided. Each has a rubber base over which aluminum oxide abrasive paper is stretched. The block is drawn back and forth from edge to edge across the test surface while water is applied. This is continued until the coating begins to show wear through to the substrate. The number of back and forth cycles to reach this end point is taken as a measure of abrasion resistance.

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Dynamic Mechanical and Tensile Properties

by Loren W. Hill[1]

DYNAMIC MECHANICAL AND TENSILE PROPERTIES are determined in all branches of materials science. There is a large body of published structure/property information that can be integrated with coatings research and development. By using structure/property information, coatings chemists can design and optimize chemical structures of the binder components of coatings. Purposeful and enlightened formulation with well-designed components makes it possible to obtain desirable coatings performance in many cases.

Determination of dynamic mechanical and tensile properties requires the use of free films. This requirement is a serious limitation because many, if not most, of the performance properties of coatings are influenced by coating-substrate interactions. Therefore, tests of coatings intact on their end-use substrates must be thoughtfully coupled with free film determinations. The practical utility of basic methods described in this section is greatly enhanced when results are interpreted in relation to results of adhesion, abrasion, hardness, flexibility, toughness, and internal stress tests as described elsewhere in the manual.

Dynamic mechanical analysis (DMA) and stress-strain analysis (SSA) of tensile properties are complementary methods in several ways. DMA involves very small strains, whereas SSA involves the maximum strain that the sample can withstand. Since the small strains used in DMA usually do not exceed the tensile strength or yield strength of the sample, the method is nondestructive. This feature facilitates property determination over a wide temperature range on a single sample, that is, DMA is often used as a temperature-scanning method. In contrast, SSA data are usually obtained at a single temperature, preferably on an instrument located in a controlled temperature and humidity room. Since the sample is broken in each test, it is very arduous to carry out SSA over a wide temperature range, and SSA is not amenable to temperature scanning.

DEFINITIONS

Tensile Versus Shear Tests

Two types of deformation of a block-shaped sample are depicted in Fig. 1. These deformations are used frequently in property determinations because they can be carried out reproducibly and treated by simple mathematics. In a tension test (Fig. 1*A*), the sample is pulled apart with straight line application of force, called "uniaxial extension." In a shear test (Fig. 1*B*), one face of the cube is held stationary and the sample is pushed sideways by application of force at the opposite face. Note that different symbols (ϵ epsilon or γ gamma) are used for strain in these two tests. A single symbol is used for stress (σ sigma), but subscripts indicate the type of test. In Fig. 1, F is force and A, B, and C are initial sample dimensions. The product $A \times B$ is the initial cross-sectional area.

It is evident in Fig. 1 that strain is defined quite differently in tension and shear tests. In a tension test, strain is the fractional increase in sample length. In a shear test, strain is the distance moved by the movable face divided by sample thickness, i.e., the distance between the stationary and movable faces. In both tests, stress is force divided by cross-sectional area, and modulus is stress divided by strain. Since strain is unitless, stress and modulus have the same units (force/area). It is evident in Fig. 1*A* that cross-sectional area will decrease as ΔC increases. If the initial cross-sectional area is used to calculate σ_t, the resulting E is called "engineering" modulus. If the change in cross-sectional area is incorporated in the calculation, the resulting E is called "true" modulus.

The relationship between tensile modulus and shear modulus is

$$E = 2(1 + \mu)G \tag{1}$$

where μ is Poisson's ratio [*1,2*]. For materials that do not undergo change in volume with strain, $\mu = 0.5$, and Eq 1 becomes $E = 3G$. Experimentally, μ is very close to 0.5 for rubbery materials and slightly less than 0.5 for many thermoplastic polymers [*1,2*].

Definitions of Dynamic Properties

In dynamic testing, an oscillating strain is applied, and the resulting oscillating stress is measured, or conversely an oscillating stress is applied, and the resulting oscillating strain is measured. Definitions and mathematical treatments do not depend on which of these modes of operation is used. Relationships between strain, stress, and time are sketched in Fig. 2 for tensile DMA with application of strain and measurement of stress. The maximum applied strain is ϵ_0. The maximum resulting stress is $\sigma_{t,0}$. Oscillation is depicted as a sine wave, but whether or not the driver of the instrument in use actually delivers a sine wave oscillation may depend on the particular instrument. The sample is held under sufficient

[1]Monsanto Co., Springfield, MA 01151.

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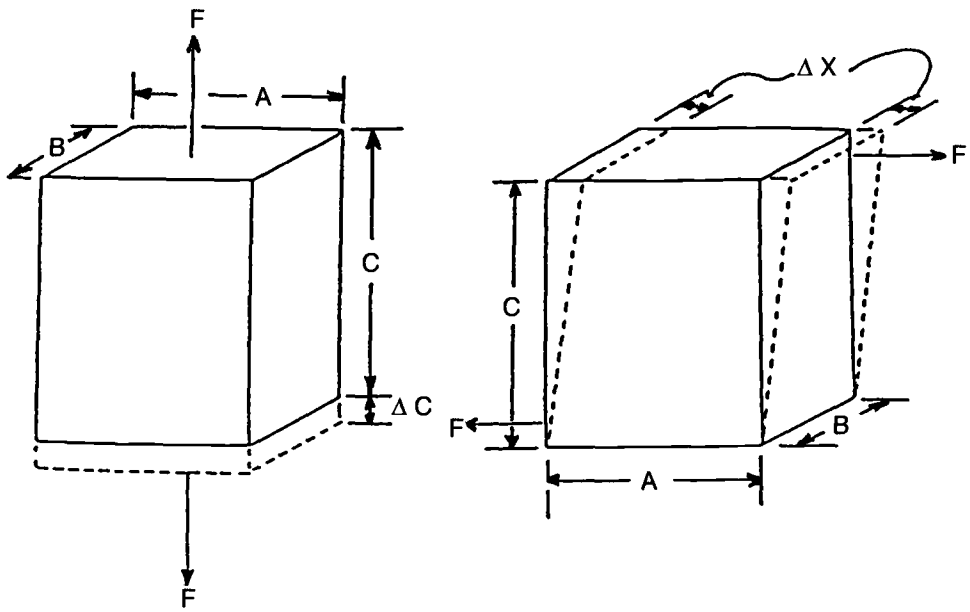

A. TENSILE

ϵ = Tensile Strain

σ_t = Tensile Stress

$$\epsilon = \frac{\Delta C}{C}$$

$$\sigma_t = \frac{F}{A \times B}$$

E = Tensile Modulus

$$E = \frac{\sigma_t}{\epsilon}$$

B. SHEAR

γ = Shear Strain

σ_s = Shear Stress

$$\gamma = \frac{\Delta X}{C}$$

$$\sigma_s = \frac{F}{A \times B}$$

G = Shear Modulus

$$G = \frac{\sigma_s}{\gamma}$$

FIG. 1–Deformations of test samples: *A.* tensile, *B.* shear. The two types of deformation have different definitions and different symbols for strain, stress, and modulus.

tension so that it remains taut (not slack) even when the oscillating strain is at a minimum.

The sine waves for strain and stress have the same frequency, but for viscoelastic samples the waves are out of phase by an amount, δ, called the phase lag. Theoretically and experimentally, δ is zero for an ideal (Hookean) elastic solid. If an ideal (Newtonian) liquid could be tested in this way, δ would be 90°. For viscoelastic materials, δ lies between 0 and 90°, and the value of δ is a rather direct indication of viscoelastic character [*1–4*].

Definitions of dynamic properties depend on the concept of resolving the stress wave of Fig. 2 into two waves, one that is in phase with strain and one that is 90° out of phase with strain. The in-phase resolved plot represents elastic response, and the 90° out-of-phase resolved plot represents viscous response. In terms of modulus, the separated responses result in the following definitions

$$\text{Tensile Storage Modulus} = E' = \frac{\sigma_{t,0} \cos\delta}{\epsilon_0} \tag{2}$$

$$\text{Tensile Loss Modulus} = E'' = \frac{\sigma_{t,0} \sin\delta}{\epsilon_0} \tag{3}$$

$$\text{Loss Tangent} = \frac{E''}{E'} = \tan\delta \tag{4}$$

The term "storage" is associated with the elastic part of the response E' because mechanical energy input to elastic materials is "stored" in the sense of being completely recoverable. The term "loss" is associated with the viscous part of the response E'' because mechanical energy input to ideal liquids is totally lost through viscous heating. The ratio E''/E' is viscous response expressed relative to elastic response. This ratio reduces to $\sin\delta/\cos\delta$, which is $\tan\delta$. Thus, the name "loss tangent" is appropriate.

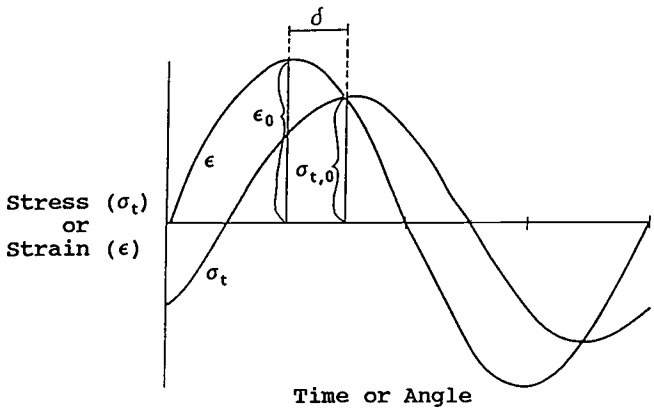

FIG. 2—Applied oscillating strain (ϵ) and resulting oscillating stress (σ_t) in a dynamic mechanical analysis experiment with tensile deformation. The phase lag (δ) and maximum values of strain (ϵ_0) and stress ($\sigma_{t,0}$) are indicated.

A check of limiting values of δ is consistent with assignment of elastic and viscous responses in Eqs 2 and 3. When $\delta = 0°$, $\cos\delta = 1.0$ and $\sin\delta = 0$. By Eq 3, E'' is zero and all of the response is elastic, i.e., E' from Eq 2. When $\delta = 90°$, $\cos\delta = 0$ and $\sin\delta = 1.0$. Now E' is zero by Eq 2 and all of the response is viscous, i.e., E' from Eq 3.

DMA relationships in Eqs 2 and 3 relate directly to characterization of samples that are solid or semi-solid. Other objectives of DMA include following viscosity and elasticity changes as the cure of thermoset coatings takes place and determining the melt-flow properties of powder coatings before the onset of cross-linking. When viscous response is the main interest, DMA is often carried out in shear.

The treatment for shear DMA is identical, but with selection of appropriate shear symbols from Fig. 1, the definitions are

$$\text{Shear Storage Modulus} = G' = \frac{\sigma_{s,0}\cos\delta}{\gamma_0} \tag{5}$$

$$\text{Shear Loss Modulus} = G'' = \frac{\sigma_{s,0}\sin\delta}{\gamma_0} \tag{6}$$

$$\text{Loss Tangent} = \frac{G''}{G'} = \tan\delta \tag{7}$$

Once the experimenters have values of $\sigma_{s,0}$, γ_0, and δ in hand, it is their choice whether to express results in terms of modulus values, Eqs 5 and 6, or in terms of "dynamic viscosity." For dynamic viscosity, the frequency of oscillation, ω in radians per second, is required, but this frequency is usually known. The frequency is required because viscosity is (shear stress)/(rate of shear strain). In a dynamic shear test, rate of shear strain is the product $\omega \times \gamma$. Definitions of dynamic viscosity are

$$\text{Dynamic Loss Viscosity} = \eta' = \frac{G''}{\omega} = \frac{\sigma_{s,0}\sin\delta}{\omega\gamma_0} \tag{8}$$

$$\text{Dynamic Storage Viscosity} = \eta'' = \frac{G'}{\omega} = \frac{\sigma_{s,0}\cos\delta}{\omega\gamma_0} \tag{9}$$

$$\text{Loss Tangent} = \frac{\eta'}{\eta''} = \tan\delta \tag{10}$$

In the Newtonian liquid limit ($\delta = 90°$), η'' is zero by Eq 9, and all of the response is viscous, η' from Eq 8. Furthermore in this limit, G' is zero by either Eq 9 or Eq 5, and the viscous response could alternatively be expressed in terms of G'' from Eq 6. Thus, in dynamic shear tests, modulus and viscosity determinations are one and the same experiment. Usually experimenters will choose Eqs 5 and 6 when the sample has a lot of elastic character and only a little viscous character, whereas the logical choice for mainly viscous materials having only a little elastic character will be Eqs 8 and 9. In principle, it would be valid to express tensile DMA results in terms of dynamic viscosities as well. This is not done very often, probably because viscosity is strongly associated with shearing experiments, not with tensile experiments. The close association of viscosity with shear is the basis for omitting the word "shear" at the left in Eqs 8 and 9.

The relationships between modulus values defined in Fig. 1 and the dynamic modulus values are [*1–4*]

$$E^2 = E'^2 + E''^2 \tag{11}$$

$$G^2 = G'^2 + G''^2 \tag{12}$$

Use of complex numbers and quantities such as $i = \sqrt{-1}$ has been avoided here. If readers would like definitions of such quantities as the "complex tensile storage modulus," E^*, they should consult Refs *1–4*. Complex notation may be convenient for mathematical derivations, but complex modulus values, with their imaginary parts, add little or nothing to the interpretation of structure/property relationships.

Definitions of Tensile Properties

The term "tensile properties" logically refers to all properties that can be determined in tests that involve tensile deformation as depicted in Fig. 1*A*. Common tests that involve tensile deformation include stress-strain tests, creep tests, and stress relaxation tests. Stress-strain tests are used much more frequently than the others. Therefore, the terms "tensile properties" and "stress-stain properties" are often used interchangeably. Creep and stress-relaxation tests are sometimes referred to as "transient tests" because responses, either elongation or stress, change with time and are determined as a function of time [*5*].

Terminology, definitions, and symbols for stress-strain tests have been taken from an earlier edition of the *Paint Testing Manual* [*6*] and from several ASTM standards:

D 2370	Test Method for Tensile Properties of Organic Coatings
D 638M	Test Method for Tensile Properties of Plastics (Metric)
D 882	Test Method for Tensile Properties of Thin Plastic Sheeting
D 412	Test Methods for Vulcanized Rubber and Thermoplastic Rubbers and Thermoplastic Elastomers—Tension
D 883	Terminology Relating to Plastics

In a stress-strain test, the sample is elongated at constant rate. The force, also called "load," required to maintain constant rate of elongation is determined. Force is converted to tensile stress (σ_t) by division by the initial cross-sectional area ($A \times B$ in Fig. 1*A*). Results are presented as a plot of stress (σ_t)

on the vertical axis versus strain (either ϵ or $100 \times \epsilon = \%$ elongation) on the horizontal axis. A hypothetical example is shown in Fig. 3 [5,6]. The tensile modulus (E) is the slope of the initial, linear portion of the plot (see Fig. 3). If the initial part of the plot is not linear, several calculations for estimating E have been suggested in ASTM D 638M. Use of the slope for E amplifies the simple definition of tensile modulus given in Fig. 1A. Other terms used for tensile modulus include "elastic modulus," "Young's modulus," and "stiffness."

The first point on the plot of Fig. 3 where the slope is zero is called the "yield point." Strain at the yield point is called "elongation at yield" (ϵ_Y). Stress at the yield point is called "yield strength" (σ_Y). Elongation is continued until the sample breaks. Strain at the break point is called "elongation at break" (ϵ_B). Stress at the break point is called "tensile strength" (σ_B) as shown in Fig. 3. However, in some cases (not shown) the stress is higher at the yield point than it is at the break point. In such cases, ASTM standards specify that the "tensile strength" be indicated as the higher value of stress and be designated as "tensile strength at yield." Practice is not uniform with regard to this latter "tensile strength" terminology.

Results of transient tests have not frequently been published for coatings. Such tests clarify viscoelastic character quite directly. Possibly unexpected field failures of coatings could be avoided in some cases if more attention were given to viscoelasticity. Only the most simple form of retardation and relaxation concepts are treated here.

In a tensile creep experiment, the sample is subjected to constant stress, σ_t, and elongation is determined as a function of time, $\epsilon(t)$. Analysis of dependence of elongation on time yields "retardation time," τ (tau). The simplest mechanical model that permits definition of τ is the Maxwell model as shown in Fig. 4. This model consists of a series connection of an ideal Hookean spring of modulus, E, and a dashpot that contains an ideal Newtonian liquid of viscosity, η. As indicated in Fig. 4, τ is the viscosity of the liquid in the dashpot

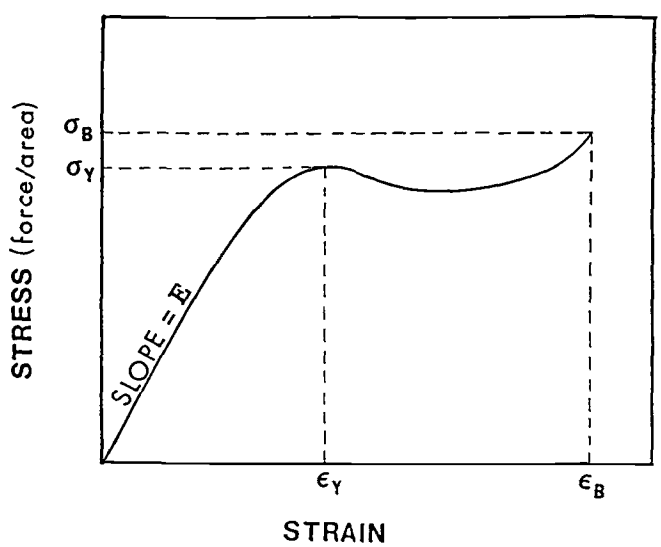

FIG. 3–A hypothetical stress-strain curve for a ductile film. Tensile properties are defined: tensile modulus (E), elongation at yield (ϵ_Y), elongation at break (ϵ_B), yield stress (σ_Y), and tensile strength (σ_B).

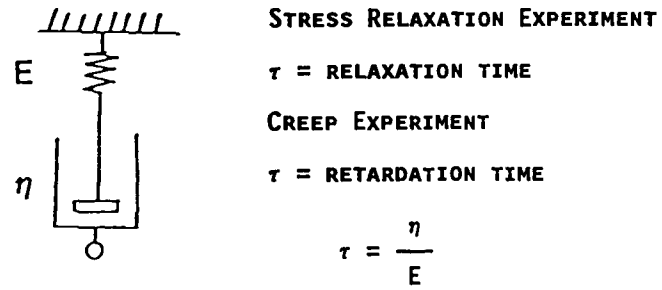

FIG. 4–A mechanical model consisting of a spring and a dashpot permits definition of relaxation time and retardation time.

divided by the modulus of the spring. Tau has units of time. Results of the creep experiment for the Maxwell model can be expressed as

$$\epsilon(t) = \epsilon(0) + \frac{\epsilon(0)}{\tau} t \tag{13}$$

When stress is first applied, the spring extends instantaneously by an amount $\epsilon(0)$. Then retarded further elongation takes place due to flow in the dashpot. It is evident in Eq 13 that the retarded elongation is linear with time. The value of τ can be obtained from the product (reciprocal of the slope) $\times$ (intercept) [4,5].

In a tensile stress relaxation experiment, the sample is elongated instantaneously by an amount ϵ, and thereafter ϵ is held constant. Stress is determined as function of time, $\sigma(t)$. Analysis of the dependence of stress on time yields "relaxation time," τ. For the Maxwell model, τ values are the same whether from creep or relaxation. For real materials, experimentation is required to determine whether or not retardation and relaxation values are equal. Results of the stress relaxation experiment for the Maxwell model can be expressed as

$$\sigma(t) = \sigma(0)e^{-t/\tau} \tag{14}$$

When the instantaneous elongation is applied, the time zero response is entirely in the spring. Then the dashpot extends with time relieving stress on the spring. It is evident from Eq 14 that the value of τ can be obtained as the time at which stress has been reduced to $1/e$ (0.368) of its initial value. Alternatively, one can obtain the value of τ from the negative of the reciprocal of the slope of a plot of $\ln \sigma(t)$ versus t [4,5].

To represent mechanical response of viscoelastic polymeric materials, it is usually necessary to use more elaborate mechanical models and to replace a single value of τ by "a spectrum of relaxation times" [1,2].

PREPARATION OF FREE FILM SAMPLES

Methods for preparation and cure of adherent films are described elsewhere in the manual and in ASTM Test Methods for Producing Films of Uniform Thickness of Paint, Varnish, and Related Products on Test Panels (D 823-87). Since dynamic mechanical and tensile property determinations require free films, ASTM Practice for Preparation of Free Films of Organic Coatings (D 4708-87), is also very useful. Details

concerning thickness measurements, which are required for calculation of cross-sectional area, are given in ASTM Test Method for Measurement of Dry-Film Thickness of Organic Coatings Using Micrometers (D 1005).

The most widely used method for free film preparation involves application on release substrates, i.e., low surface energy substrates. Four release substrates are described in ASTM D 4708-87. Low surface energy results in poor adhesion so that the coating can be stripped from the release substrate after it is cured. Surface tension differences between the coating and release substrate must be carefully balanced. If the surface tension of the liquid coating is higher than the critical surface tension of the release substrate, the coating will crawl inward from the edges to give nonuniform thickness. In extreme cases of crawling, the coating will break up into unconnected puddles. There are many types of release paper and many surface treating agents to convert glass or metal panels into low-energy surfaces. It is worthwhile to try several release surfaces to find the balance which will avoid crawling but will still permit separation. Tendency to crawl can be reduced by use of high-viscosity formulations. Viscosities for draw-down application (see ASTM D 823-87) can be quite high compared to those required for spray application.

The second most widely used method for preparation of free films involves amalgamation of tin by mercury. ASTM D 4708-87 describes use of 25-μm-thick dental tin foil. The foil is smoothed onto glass plates before application of the coating. In our laboratory we have used 7.6 by 15.2-cm (3 by 6-in.) tin-plated steel panels (Type DT panels, Q-Panel Co.) The tin plate on the panels amalgamates much more quickly than that on tin-plated food can stock. After the coating is cured, the panel is placed in a wide-mouth quart jar containing mercury to a depth of only 0.64 to 1.3 cm (1/4 to 1/2 in.). The jar is tightly capped during amalgamation. During a period of one and one half to two days, mercury creeps up the panel underneath the coating as tin is amalgamated. After the film is completely freed from the substrate, it can be lifted off and wiped to remove mercury. The amalgamation procedure is best carried out in a hood reserved for this purpose. The work surface of the dedicated hood can consist of a metal grid mounted 1.3-cm (1/2 in.) above a shallow tray that contains sulfur. Other safety precautions include careful attention to panel handling procedures and disposal procedures, frequent monitoring of air flow velocities, use of protective gloves, and mercury vapor monitoring devices. Danger of exposure to mercury vapor has resulted in prohibition of amalgamation methods in some coatings laboratories.

Thickness is an important consideration in preparation of samples for dynamic mechanical and tensile property tests. Usually tests are more reproducible if samples are thicker than normal coatings thicknesses. However, film formation seldom occurs in exactly the same way for thick films as for thin ones. Several reasons for dependence of cured film properties on thickness have been discussed [*5*]. In our laboratory, films of 1 mil (25 μm) and up have been analyzed routinely. It has not been possible to analyze or even handle very thin free films such as beverage can coatings which are approximately 3 to 5 μm thick.

Coatings and thin plastic film samples are usually prepared as rectangular strips, whereas thicker materials are prepared as dogbone-shaped samples. The narrowing in the middle of the dogbone tends to control where failure occurs in tension tests, but for thin samples this narrowing causes the cross-sectional area to be too small for many load measuring cells. The dogbone shape also provides more area for clamping which facilitates the balance between slip-free clamping and avoidance of rupture at the clamp.

There is extensive literature on the notch sensitivity of polymeric materials in stress-strain tests [*7*]. The challenge in preparation of high *Tg* coating samples is to avoid undesired notches, nicks, or cracks along the edges. Small edge cracks, which are very difficult to detect even with magnification, can cause premature failure in tension tests. Usually samples are die cut, and the sharpness and condition of cutting edges of the die affect uniformity of sample edges.

DETERMINATION OF DYNAMIC PROPERTIES

Description of Dynamic Mechanical Analysis (DMA)

One of the reasons for rapidly expanding use of DMA for coatings and other research is the availability of automated and computer-controlled instrumentation. Automated instruments and the suppliers of these instruments are listed in Table 1 [*4*]. A common feature of all these instruments is oscillatory deformation, an example of which is shown in Fig. 2. Variable features include: the type of deformation (tensile, shear, or poorly defined), free versus forced oscillation, frequency scan versus temperature scan versus either, sensitivity for thin film analysis, capability of transversing the entire range of property behavior (glassy to transition to rubbery) during a single temperature scan, breadth and rate of temperature scan, breadth and rate of frequency scan or range and number of frequency settings, versatility of sample holding devices, ruggedness versus flimsiness, amount of attention required once a run has been started, accuracy and versatility of the associated software for control during the run and data treatment and plotting after the run. In several cases, newer models permit determination of properties at several fre-

TABLE 1—Automated DMA instruments.

CSL Rheometer—Carri-Med
Dynamic Mechanical Analyzer, DMA 442—Netzsch
Dynamic Mechanical Analyzer, DMA 7—Perkin-Elmer
Dynamic Mechanical Analyzer, DMA 983—TA Instruments
Dynamic Mechanical Rheological Inst., RPA 2000—Monsanto
Dynamic Mechanical Thermal Analyser—Polymer Labs
Dynastat/Dynalyzer—Dynastatics/Imass
Mechanical Spectrometer; RMS 800, RDS II, RDA—Rheometrics
Rheolab MC 20—Physica
Rheovibron/Autovibron—Imass
Rheovibron DDV-II-C, Automated—Orientec
Servo-Hydraulic Machine—Instron
Solids Analyzer, RSA II—Rheometrics
Torsional Braid Analyzer—Plastics Analysis Instruments
Torsionautomat—Brabender
Viscoanalyser—Indikon/Metravib
VOR Rheometer—Bohlin
Weissenberg Rheogoniometer—Carri-Med

NOTE: In addition, several thermo-mechanical analysis instruments have an option of oscillatory loading of the TMA probe.

quencies during a single temperature scan. Although it is necessary to use a rather low temperature scan rate in multiple frequency runs, the amount of data obtained is remarkable. Chances of acquiring an instrument that will actually function well in the intended experiments are greatly increased by asking suppliers about these variable features.

The procedure for carrying out a DMA run on an automated instrument is rather simple, with details depending on the particular instrument. Usually the associated software includes a "run" program which prompts the operator to input sample data (e.g., thickness) and settings for the run such as initial and final temperatures, frequency of oscillation, heating rate, etc. After the input steps, there is usually a cooling period. The instrument takes over when the preset initial temperature is reached. Thereafter nothing is required of the operator until the run is finished. Usually initial and final temperatures are selected to span the glassy region, transition region, and rubbery plateau region. For direct tensile DMA, the run program usually contains a tensioning subroutine, which provides constant static tension sufficient to avoid slack in the sample in the glassy region and then decreasing static tension as the sample softens in the transition region. Modification of the tensioning sub-routine is often necessary. If tension is too high, films break in the glassy region or are pulled apart in the transition region. If tension is too low, slack results or the oscillatory stress falls below measurable values. Skilled operators soon develop several modified run programs with different tensioning parameters that are suitable for samples of various properties and dimensions.

Various support materials, such as glass braids and metal springs or shims, are used when the sample is a viscous liquid and the objective is to follow cure as the coating formulation is converted to a solid. Use of supports makes it difficult to obtain absolute values of E', but relative values are often sufficient for component optimization. The position of peaks in E'' or tanδ plots are usually not shifted when a support is used. When coating samples do not contain solvents, e.g., powder coatings and 100% active coatings, parallel plate, and cone and plate geometries can be used.

In some cases, DMA is treated as an adjunct to thermomechanical analysis (TMA). The TMA probe is driven up and down in an oscillatory manner as temperature is scanned. General indications of liquid-like character during transitions can be obtained, but quantitative DMA data are not often obtainable in this manner.

Interpretation of DMA Plots

DMA plots are shown in Fig. 5 for a clear film prepared from an acrylic polyol (ACR) and an etherified melamine formaldehyde (MF) cross-linker. Plots are labeled according to Eqs 2, 3, and 4. The storage modulus level at the left is typical of amorphous, unpigmented films in the glassy state. The 25°C data are of interest for comparison with modulus values obtained from the slope of stress-strain plots because SSA is usually carried out at 25°C. The value of E' (25°) from the computer printout corresponding to Fig. 5 is 1.38×10^{10} dynes/cm^2. The same value expressed in other units is 1.38×10^9 Pa or 2.00×10^5 psi (1 pascal = 1 newton/m^2 = 10 dynes/cm^2 = 1.45×10^{-4} pounds-force per square inch). The recommended SI unit is Pa. The value of E'' (25°) is 6.86×10^8 dynes/cm^2. Inserting E' and E'' (25°) values into Eq 11 and solving for tensile modulus, E, we obtain $E = 1.382 \times 10^{10}$. In this case $E = E'$ (25°) to a very close approximation, and the contribution of E'' (25°) to E is negligible. Hard, tough coatings often have tensile modulus values from SSA ranging from 1×10^{10} to 3×10^{10} dynes/cm^2 [*5,7,8*], in agreement with the DMA value. For a quantitative comparison of E from SSA and E from DMA via Eq *11*, the strain rate from SSA would have to be matched with the oscillating frequency from DMA.

The viscous response is not always negligible relative to elastic response, of course. The E'' contribution is highest at the temperature of the maximum in tan delta, 79°C in Fig. 5. Note that E' (79°) is 1.04×10^9 dynes/cm^2, and E'' (79°) is 5.15×10^8 dynes/cm^2. From Eq *11*, $E = 1.16 \times 10^9$ dynes/cm^2, and $E > E'$ (79°) for this case. If we actually carried out SSA at 79° and a strain rate corresponding to 11 Hz, we would expect to find $E = 1.16 \times 10^9$ dynes/cm^2. During the elongation in SSA it would not be evident that a significant fraction of the resistance was viscous in nature. However, after the sample broke or was released from the grips, retraction would be delayed (not instantaneous) and part of the deformation would be permanent.

The middle portion of the plots in Fig. 5 represents the transition region where E' drops sharply and both E'' and tanδ go through a maximum. The glass transition temperature, *Tg*, is usually taken as the temperature of the maximum in the tanδ plot, 79° in Fig. 5. Some users of DMA prefer to define the temperature of the maximum in the E'' as *Tg*, 55° in Fig. 5. The lower *Tg* value agrees more closely with that obtained from differential scanning calorimetry, but the higher value can be obtained with better reproducibility because the tanδ peak is sharper than the E'' peak. Regardless of the data point selected to express *Tg*, it is important to remember that *Tg* depends on rate of testing for viscoelastic materials.

The effects of changing rate of testing, i.e., frequency in DMA, are shown in Table 2. The 11 Hz data of Table 2 correspond to the run depicted in Fig. 5. A ten-fold increase in frequency results in a 7 to 9° increase in *Tg* with a slightly stronger dependence on frequency at the higher frequencies. In a recent review, Hartmann [*9*] noted that a 7°C *Tg* change per decade change in frequency is used as a "rule-of-thumb." Results of Table 2 are consistent with this generalization. The height of the tanδ peak is nearly independent of frequency, but the width increases with increasing frequency. Very similar dependence of height and width on frequency was observed for lightly cross-linked epoxy films [*9*]. Values of E' (min) increase slightly with increasing frequency (Table 2). The structural implications of E' (min) will be discussed in the next sub-section.

Height and width of tanδ peaks reflect structural homogeneity and cross-link density. Homogeneous, uncross-linked, noncrystalline polymeric materials of narrow molecular weight distribution usually have tanδ (max) values greater than one and sometimes greater than two. Such tanδ peaks are very narrow. A broader molecular weight distribution results in a wider peak and a lower value of tanδ (max). Introduction of cross-links invariably reduces tanδ (max) and usually increases peak width. For homogeneous cross-linked

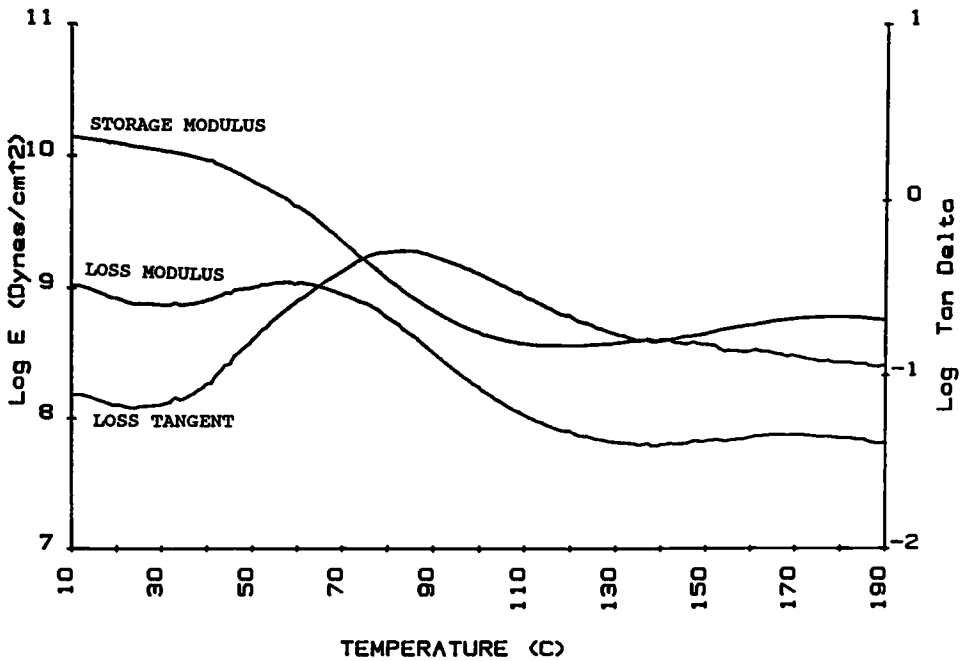

FIG. 5–DMA plots for a clearcoat prepared from an acrylic polyol (ACR) and an etherified melamine formaldehyde (MF) resin, ACR/MF 70/30. The film was cured before DMA for 30 min at 120°C with 0.5% para-toluenesulfonic acid. DMA was carried out at 11 Hz. See Table 2 for dynamic properties.

TABLE 2—Dynamic properties of acrylic/MF clearcoat.

Frequency, Hz	*Tg*, °C	Tanδ, max	*PW*,[a] Δ, °C	*E'*, (min), dynes/cm^2	Temperature of *E'* (min), °C
3.5	76	0.49	45	3.3×10^8	108
11.0	79	0.49	50	3.6×10^8	112
35.0	83	0.52	55	4.2×10^8	116
110.0	88	0.52	59	4.7×10^8	121

[a]*PW* is peak width at half height.

samples, peak width reflects the broadness of the distribution of lengths of chains between junction points in the network [*2,3*]. For sound and vibration damping, materials with both high and wide tanδ peaks would be desireable, but height and width cannot be adjusted independently [*9*]. High peaks tend to be narrow, and wide peaks tend to be low. These observations have resulted in speculation concerning a general comparability of peak areas of the glass transition. Eventually theoretical treatment of peak areas may prove to be useful for structure/property correlations.

Samples that undergo partial phase separation during molecular weight buildup and cross-linking often have very broad transitions [*4,9,10*]. Manson and Sperling [*10*] have described the use of interpenetrating polymer networks to limit and control the extent of phase separation. When *Tg* values of the separate domains are close to one another, a general broadening is observed. When *Tg* values of the separate domains are considerably different, tanδ plot shapes provide considerable structural information. Observation of two narrow peaks with low tanδ values between them indicates distinct phase separation with little mixing at domain boundaries. Observation to two broad and indistinct peaks with high tanδ values between them indicates diffuse domains with extended regions of varying composition at the boundaries [*4,10*]. Diffuse domains have also been created in multiblock uncross-linked polymers, and block design has resulted in controlled broadening of tanδ peaks [*11*].

The relationships between transition width and coating end-use performance have been presented for radiation-cured coatings [*12*], polyol/melamine thermoset coatings [*13,14*], gel coats [*14*], and can coatings [*14*]. Although the glass transition is emphasized in this section, many polymers are known to have multiple transitions. Low-temperature transitions are observed in DMA as tanδ or *E"* peaks that are quite small compared to the glass transition peaks. As discussed in the section entitled **Relationship to Other Mechanical Properties,** good impact resistance is often attributed to transitions that produce low-temperature loss peaks.

Interpretation of tanδ peak broadening in terms of structural nonuniformity requires considerable restraint because in some cases broadening is caused by physical or chemical changes that take place during the temperature scan. In some cases, DMA has its own uncertainty principle; the structural features that are under study are changing during the determination. Physical changes include loss of plasticizer or absorbed water and morphological changes

such as partial crystallization. Chemical changes include additional cross-linking of thermoset coatings during the scan and oxidative or thermal degradation. In general, if the temperature of processing the samples is well above the temperature of the tanδ peak under analysis, there is much less chance that properties are changing during the scan.

Determination of Cross-Link Density

For unpigmented, cross-linked coating films, the level of storage modulus, E', in the rubbery plateau region above Tg is an indication of cross-link density. A wide range of variation has been observed from approximately 4×10^7 dynes/cm^2 for lightly cross-linked films to approximately 2×10^9 dynes/cm^2 for very highly cross-linked films. Increases in E' values in the rubbery plateau have been attributed to increases in cross-link density for many types of studies: increasing cure temperature and cure time [*13,16–18*], increasing radiation dose in electron beam curing [*15*], increasing the stoichiometric balance in epoxy films [*2,19*] and in polyol/melamine films [*13,17,18*], increasing the functionality of the cross-linker in radiation cure films [*20*] and in powder coatings [*21,22*], and increasing the molecular weight of the main film former in acrylic clearcoats [*23*].

Quantitative aspects of the relationship between E' in the rubbery plateau and cross-link density have recently been clarified [*18*]. Cross-link density is defined as

$$\nu_e = \text{moles of elastically effective network chains per cubic centimeter of film} \quad (15)$$

Cross-link density can be calculated using Eq 16

$$\nu_e = \frac{G'}{RT} = \frac{E'}{3RT} \quad (16)$$

where the storage modulus values, G' or E', are obtained in the rubbery plateau, T is temperature in degrees K corresponding to the storage modulus value, and R is the gas constant (8.314×10^7 dynes/degrees K · mole in the cgs unit system). Inserting the 3.5 Hz data from Table 2 ($E' = 3.3 \times 10^8$ dynes/cm^2 and T = 108°C = 381°K) into Eq 16 gives $\nu_e = 3.47 \times 10^{-3}$ moles/cm^3. Since Eq 16 has no correction for frequency dependence of E', a more accurate value would be obtained if frequency were reduced until E' no longer depended on frequency. Extrapolation to zero frequency was used in cross-link density calculations for powder coatings [*21*]. For a polyurethane film of low Tg but relatively high cross-link density, E' plots were identical in the rubbery plateau at 11 and 110 Hz [*18*]; thus, no frequency extrapolation was necessary for this case.

Equation 16 has been called "the ideal network law" with an analogy implied to the ideal gas law [*18*]. In an ideal network, all chains are elastically effective. Conversion in the network forming reaction is complete, and there are no small loops or dangling ends. For ideal networks formed by functional group reactions of terminally functional (telechelic) starting materials, the value of ν_e can be calculated directly from Eq 15. The calculation requires only a balanced chemical equation and an experimental determination of cured film density. For example, consider a tetrafunctional coreactant B_4 (M_n = 3000) cured by a trifunctional cross-linker A_3 (M_n = 300)

$$4A_3 + 3B_4 \longrightarrow \text{Ideal Network (density} = 1.10\ \text{g/cm}^3)$$

The mass of the network formed by this reaction is 10 200 g (3 × 3000 + 4 × 300), and the volume is 10 200/1.10 = 9273 cm^3. This volume of cured film contains 24 mol of chain ends (4 × 3 + 3 × 4) coming into junction points in the network. By definition, a chain has two ends; therefore, there are 12 mol of elastically effective chains in 9273 cm^3 of ideal network film. From Eq 15, $\nu_e = 12/9273 = 1.29 \times 10^{-3}$ mol/cm^3.

Equation 17, attributed to Scanlon [*18,24*], formalizes this type of calculation

$$\nu_e = \frac{3}{2}C_3 + \frac{4}{2}C_4 + \frac{5}{2}C_5 + \cdots = \frac{1}{2}\sum_{f=3}^{\infty} fC_f \quad (17)$$

where C_f is the concentration of "f" functional reactant expressed in unusual units, i.e., moles of reactant per cubic centimeter of *final film*. Difunctional reactants contribute to volume but do not increase the number of moles of chains. Therefore, there is no C_2 term in Eq 17.

Ideal network calculations have been carried out for several types of coatings such as polyester polyol/melamine films [*17*], epoxy/diamine films [*19*], and powder coating films [*21,22*]. The ν_e values calculated from reactant structures agree remarkably well with experimental ν_e values from Eq 16.

Although ν_e is useful for network characterization, most coating chemists can more easily visualize a network based on the value of M_c

$$M_c = \text{weight of sample in grams that contains one mole of elastically effective chains} \quad (18)$$

If chain lengths in the network vary, one can place a bar over M_c and refer to this quantity as "number average molecular weight of effective network chains." Based on Eqs 15 and 18, the relationship between ν_e and M_c is

$$M_c = \frac{\rho}{\nu_e} \quad (19)$$

where ρ is film density in g/cm^3. For the $4A_3 + 3B_4$ example, $M_c = 1.10/1.29 \times 10^{-3} = 853$ g/mol. For the film of Table 2, the experimental density is 1.12 g/cm^3, and M_c is $1.12/3.47 \times 10^{-3} = 323$ g/mol. Of course, a high value of M_c corresponds to a loose network and a low value to a tight network.

Equation 16 can be considered empirical or the result of kinetic theory of rubber elasticity [*20,24-28*]. The theory was developed for networks that have very long chains between junction points. For long chains, conformations can be treated by statistical-mechanics concepts. The chains in networks of greatest interest for coatings are much too short for such treatments. For long chains between junction points, results of the theory are often expressed as [*20*]

$$\nu_e = \nu_c + \nu_p = \frac{G}{gRT} \quad (20)$$

where ν_e is sum of a chemical contribution, ν_c, and a physical contribution, ν_p. The physical contribution is attributed to chain entanglements [*28*] or physical constraints [*25–27*]. The factor, g, is related to junction point displacement under stress and is reported to depend on functionality [*20,25*]. If the reader chooses to use rubber elasticity theory, Eq 16 is

obtained from Eq 20 with $g = 1.0$, $G = G'$, and $\nu_p = 0$ (relative to ν_c).

A new theory is needed that results in Eq 16 by consideration of entropy of conformations of short chains. This approach would avoid applying long chain theory to material having short chains.

Relationship to Other Mechanical Properties

Knowledge of dynamic properties is useful for optimizing the chemical structure of coatings components. When the binder is a copolymer, monomer ratios can be altered to control *Tg*. In thermosets, increasing the functionality of the cross-linker is expected to cause an increase in cross-link density. DMA is a very direct method for determining whether purposeful structural changes have actually had the desired effects.

In addition to general structure/property uses of DMA, progress is being made in establishing relationships between dynamic properties and the results of paint test methods for hardness, flexibility, impact resistance, and solvent resistance. DMA has some inherent limitations in the establishment of these property/property relationships. The oscillatory deformation, e.g., ϵ_0 in Fig. 2, is very small. If the paint performance property depends critically on large deformations, a property/property correlation should not be expected. Results of paint performance tests usually depend to some extent on interactions between coating and substrate. When dependence on coating-substrate interactions is dominant, a free film method such as DMA should not be expected to correlate with results of paint tests.

DMA has helped elucidate the causes of reversals in rank order of hardness among films when different tests are used [*5,29*]. As described elsewhere in the manual, hardness is determined by penetration, pendulum, and scratch test methods. The most important property for influencing hardness is *Tg*. However, even for a series of films that have the same *Tg*, considerable differences are sometimes observed in hardness test results. We have observed that penetration hardness depends more directly on the E' (25°) value than on *Tg*. Films of the same *Tg* can have quite different values of E' (25°). Pendulum hardness depends more directly on E'' values than on E' values. This result is expected because damping of the swings of a pendulum depends on conversion of mechanical energy into heat through viscous effects in the coating. As noted earlier, E'' is a measure of viscous response. Films which have nearly the same E' (25°) values and the same penetration hardness can have quite different E'' (25°) values and quite different values of pendulum hardness. The back and forth rolling motion of a Sward Rocker is also damped by viscous effects, and therefore depends strongly on E'' values. In this case, there is also a contribution from sliding friction. Usually pendulum hardness is determined at a single temperature, but Sato [*29*] describes studies of damping time as a function of temperature. Plots of the reciprocal of damping time versus temperature have exactly the same shape as the tanδ plot for the same films. Both glassy and rubbery materials have low tanδ values as shown in Fig. 5. If a pendulum hardness test is carried out at room temperature on a material that is in its rubbery region at room temperature, a careless interpreter of results is likely to conclude that rubber is very hard. This example illustrates that DMA can be used to understand the results of paint tests more fully.

Among the many scratch tests that have been devised, the most widely used is pencil hardness. Although pencil hardness results are quite reproducible when carried out by one skilled in the art, these results sometimes do not correlate with either penetration or pendulum hardness results. Furthermore, there is no known dynamic property that correlates well with pencil hardness. The plowing action involved in pencil hardness failures may involve large localized deformations. A relation to stress-strain analysis, which involves large deformations, is more likely.

Flexibility of coatings is often measured by mandrel bend tests and falling weight impact tests (see a previous chapter in this book). In thermoplastic polymer studies, good flexibility and impact resistance are often associated with low temperature peaks in E'' and tanδ plots [*30*]. Rubber-toughened epoxy coatings clearly show the low temperature peak attributable to the rubber phase [*31*]. Polyester/melamine films have much better mandrel bend performance than do acrylic/melamine films of similar *Tg* and cross-link density. DMA scans beginning at −100°C show a weak tanδ peak at −70°C for the PE/MF films, but no such peak is observed for the ACR/MF films [*18*]. In some cases [*12,13*], extreme broadening of the peak in the E'' plot has been associated with improvements in flexibility of coatings.

Pigments often increase the toughness of coatings without broadening the transition or introducing low-temperature loss peaks [*15*]. The main effect of increasing pigment volume content (PVC = 0 to 55%) on DMA plots is to increase E' values moderately in the glassy region and strongly in the rubbery plateau [*15*]. Values of *Tg* often increase by about 5 to 10°C at PVC = 0.4 relative to the corresponding clear coatings [*15*].

Solvent resistance as measured in methyl ethyl ketone double rub tests is related to E' values in the rubbery plateau, i.e., to cross-link density [*5,13*]. MEK resistance also depends on the solubility parameter of the coating. Although the double rub test is widely used to determine the degree of cure of thermoset coatings, the only ASTM method adopted relates to zinc-rich primers (D 4752-87). Relationships between the number of double rubs and E' (min) values are quite reproducible within a coating type but not from type to type. For example, with acrylic clearcoats, 200 double rubs are obtained when E' (min) = 2×10^8 dynes/cm^2 [*13*]. Films of this type having 50 to 100 double rubs typically have E' (min) values in the range of 5×10^7 to 1 to 10^8 dynes/cm^2. In contrast, polyester polyol powder coatings, cured with several types of cross-linkers, yielded 200+ double rubs despite having E' (min) values as low as 5×10^7 dynes/cm^2 [*22*]. The lack of generality in the relationship of MEK resistance to E' (min) for various coatings types is believed to result in part from differences in solvent-polymer interactions. There may also be a weak dependence of MEK resistance on *Tg* as well as a strong dependence on E' (min).

DETERMINATION OF TENSILE PROPERTIES

Description of Stress-Strain Analysis (SSA)

Instrumentation for SSA is described in detail in the ASTM test methods listed in the section of this chapter entitled Definitions of Tensile Properties. In most cases, specific instruments are not identified, apparently to avoid commercial implications, but it is generally known than Instron® instruments (Instron Engineering Corp.) are widely used. For organic coatings the most suitable test method is usually ASTM D 2370. However, other tension test methods contain additional useful information. ASTM D 638M is useful for selection of metric units and units consistent with SI recommendations. ASTM D 882 has rather extensive data on statistical treatments for plastic sheeting, but the statistical methods could be beneficially applied to coatings films. For certain types of coatings, such as flexible primers or coatings for plastic substrates, rubbery behavior is expected, and ASTM D 412 provides useful information such as data treatment when a crack moves slowly across the sample as opposed to the more usual instantaneous failure mode. Often stress-strain curves do not start out with constant slope as shown in Fig. 3, but instead have an initial curvature caused by takeup of slack. The initial curved portion is called a "toe," and toe compensation is described in ASTM D 638M and in ASTM D 882. Some stress-strain curves have no linear (i.e., no Hookean) region from which to calculate the slope for modulus values. In such instances the "toe corrected" origin and another point on the curve are joined by a straight line. The slope of the line is reported as the "secant modulus." The elongation percentage at the second point selected is always reported along with the value of secant modulus. Graphical illustrations of secant modulus determinations are given in ASTM D 638M and in ASTM D 882. Among the various test methods, D 638M contains the most complete list of definitions and symbols.

Determination of "tensile energy to break" is described in ASTM D 882. The area under the stress-strain curve, e.g., see Fig. 3, is divided by sample volume to obtain this quantity, which has also been called "work-to-break" or "toughness" [5]. Recommended units are megajoules per cubic meter. ASTM D 882 describes how an integrated chart paper area (distance^2) can be converted to energy/volume by using the ordinate setting (force/distance of chart paper), the abscissa setting (distance of elongation/distance of chart paper), and the sample dimensions. Now that computers are used to control operation and to treat data for SSA [32], numerical integration is nearly instantaneous, and tensile energy to break is likely to be reported more often. This SSA property may prove to be useful for correlations with paint test results.

Interpretation of Stress-Strain Curves

Schematic stress-strain curves for various types of polymeric materials are shown in Fig. 6 [2]. This extremely wide range of property variation is represented in coatings of various types. Scales on the graphs give an order-of-magnitude indication of property values. Brittle materials (6*A*) have high

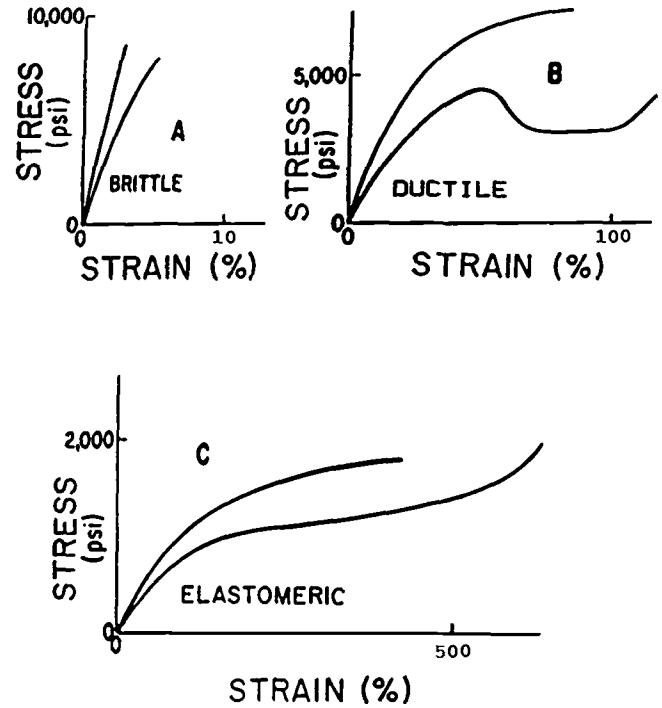

FIG. 6–General kinds of stress-strain curves for various types of coatings. Scales indicate order-of-magnitude values.

modulus values (initial slope), tensile strengths up to about 8000 psi (5.5×10^7 Pa = 5.5×10^8 dynes/cm^2), and elongations below 10%. Ductile materials (6*B*) usually have lower initial slopes, tensile strengths in the 4000 to 6000 psi range, and elongations of about 100%. The upper plot in 6*B* corresponds to yielding with uniform sample deformation between the grips. The lower plot in 6*B* corresponds to a ductile sample that necks down at the yield point, and further elongation (~40% to 110% in Fig. 6) occurs with increase in length of the necked part of the sample. Elastomeric (rubbery) samples (6*C*) have much lower initial slopes than brittle materials, tensile strengths of about 2000 psi, and elongations of the order of 400 to 500%. The upward curvature near the end of the lower plot in Part C is attributed to strain-induced crystallization [2].

Materials represented in 6*A* and 6*B* of Fig. 6 have *Tg* values above the test temperature. Therefore, modulus values depend on secondary interactions of polymer chain segments and partial crystallinity, if any exists. The elastomeric material (6*C*) has *Tg* well below the test temperature. Therefore, modulus values depend in part on cross-link density, chain entanglements, or both.

Stress-strain curves are carried out at a constant rate of strain and results depend on strain rate selected. In general, a higher rate results in higher modulus. The two curves in 6*A* could represent the same material strained at different rates. In fact a large increase in strain rate could cause the plots of 6*B* to be converted to the plots of 6*A*. Dependence on strain rate is evidence of viscoelasticity. Strain rate dependence in SSA, therefore, has the same origin as dependence on oscillatory frequency in DMA (see Table 2).

A recent study of silicone-epoxy resins cross-linked with amines of various functionality [*32*] illustrates the extreme range of stress-strain properties exhibited by coating films. Tensile strength ranged from 31 to 4418 psi. Percent elongation ranged from 7 to 177%. Unfortunately, neither modulus values nor tensile energy to break were reported. Property variations were attributed to differences in degree of entanglement and to partial phase separation. In a network-forming thermoset system, it would be impossible to get a tensile strength as low as 31 psi unless incompatibility had prevented occurrence of the network-forming reaction.

Examples of all types of behavior shown in Fig. 6 are represented in a single figure for coatings used on naval aircraft [*33*] (see Fig. 4, Ref *33*). One plot shows results for a polysulfide sealant that has a tensile strength of about 250 psi and an elongation >130%. Results for a flexible polyurethane primer are a tensile strength of 3500 psi, a yield strength of 3200 psi, an elongation at break of 90%, and an elongation at yield of 40%. The plot shows that a polyurethane topcoat yields and breaks at about the same point: 4000 psi and 22% elongation. The plot for an epoxy primer shows brittle behavior (no yield point), a tensile strength of 2300 psi, and an elongation at break of 7%. The authors [*33*] report that replacing the epoxy primer by the flexible polyurethane primer eliminated the need for the sealant coat.

SSA has been used extensively to characterize cationic UV-cured cycloaliphatic epoxy/polyol coatings [*34-36*]. The mechanism of introduction of polyol is a chain transfer step [*34*], which permits use of a wide range of epoxy:polyol ratio without need for stoichiometric balance. Selection of flexible polyols with this wide formulating latitude permits preparation of cross-linked films with an extremely wide range of mechanical properties. Numerous stress-strain curves have been presented for this type of system with oligomeric propylene oxide polyols [*35*] and with oligomeric caprolactone polyols [*36*]. Examples of stress-strain curves for a cycloaliphatic diepoxide (CYRACURE® UVR-6110, Union Carbide) and a propylene oxide triol (*MW* = 702) are shown in Fig. 7 [*35*]. The corresponding tensile properties are given in Table 3. Films from Compositions 1 through 4 all give brittle failure (compare Fig. 6*A*) and only moderate changes in tensile properties (Table 3) despite a large change in composition. At Composition 5 (70/30 epoxy:polyol, see Table 3) a yield point is first noted, and thereafter very large property changes occur despite relatively small changes in composition. Compositions in the 4 to 6 range (see Table 3) are reported to give excellent post formability, as required for coatings on beverage can ends, while maintaining adequate hardness and solvent resistance [*34-36*].

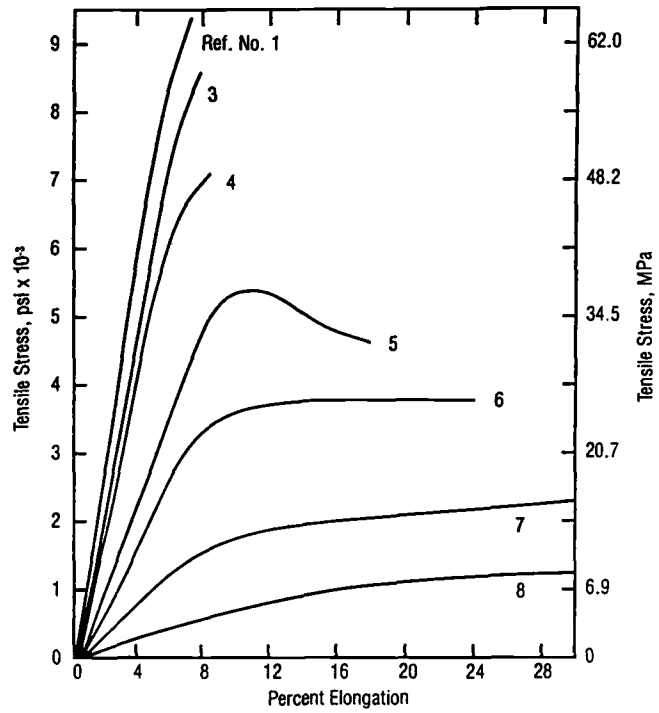

FIG. 7–Stress-strain curves for UV-cured cycloaliphatic epoxide films flexibilized with oligomeric propylene oxide triol. Strain rate is 40% per minute. See Table 3 for tensile properties.

Relationship to Other Mechanical Properties

Stress-strain analysis (SSA) is used in a general way to assess suitability of a binder for various coating end uses. Most coating chemists associate modulus with coating hardness and percentage elongation at break with coating flexibility. Quantitative correlations of these properties are not published very often, however. The lack of published correlations may result from the fact, noted above, that paint tests of adherent coatings depend on coating-substrate interactions, whereas SSA is carried out on free films. ASTM Test Method for Elongation of Attached Organic Coatings with Conical Mandrel Apparatus (D 522-88) describes how to calculate percent elongation from the crack length in a conical mandrel bend test. Comparison of elongation of adherent coatings by the conical mandrel method and elongation of the same coating as a free film from SSA would certainly be of interest, but such comparisons were not found in the literature.

The logic of associating yield behavior in SSA with post formability of coil coated metal was noted in 1977 [*37*]. In 1987, Koleske [*35,36*] confirmed that compositions that exhibited a yield point performed well in the demanding post-forming operations carried out on beverage can ends.

Evans and Fogel [*38*] provided convincing evidence that gloss retention during abrasion of floor coatings is related to the area under stress-strain curves. This area, divided by sample volume, is called "work-to-break" or "toughness" as noted in the subsection of this chapter entitled **Definitions of Tensile Properties.** The authors provide a clear example of the need to match strain rates when attempting to correlate SSA results with paint test results.

Failure of attempts to correlate pencil hardness with penetration hardness, e.g., Tukon Hardness, probably result because the former has a strong requirement for toughness, whereas the latter is more dependent on the modulus value at room temperature (see chapter subsection entitled **Relationship to Other Mechanical Properties**).

DMA is much more generally applicable to determination of cross-link density (see chapter subsection entitled **Determination of Cross-Link Density**) than is SSA. If the *Tg* of a coating binder is well below the temperature at which

TABLE 3—Tensile properties[a] of UV-cured cycloaliphatic epoxide films flexibilized with oligomeric propylene oxide triol.

Film No.[b]	Composition[c] Epoxide, wt%	Triol, wt%	Tensile Modulus,[d] psi	Tensile Strength, psi	Elongation, %
1	90.0	10.0	3.88×10^5	9.5×10^3	6.6
2	85.0	15.0	3.72×10^5	8.9×10^3	6.6
3	80.0	20.0	3.33×10^5	8.4×10^3	7.4
4	75.0	25.0	2.95×10^5	7.0×10^3	8.1
5	70.0	30.0	2.05×10^5	4.3×10^3	16.2
6	66.7	33.3	1.48×10^5	3.7×10^3	24.3
7	63.4	36.6	0.70×10^5	2.5×10^3	54.0
8	60.0	40.0	0.26×10^5	2.0×10^3	88.4

[a]Strain rate, 40% per minute.
[b]Keyed to the plots in Fig. 7.
[c]Weight % of polymeric binder. (Films also contain 2.9 wt% photoinitiator and 0.5 wt% flow agent.)
[d]1% secant modulus. (The modulus range expressed in pascals is 2.68×10^9, No. 1, to 1.79×10^8, No. 8.)

SSA is carried out, then the modulus from the initial slope of the stress-strain curve is a rubbery plateau modulus and Eq 16 is valid at least in principle. In practice, curvature in stress-strain curves and permanent deformation usually result in inappropriate modulus values. An innovative approach to avoiding the permanent deformation problem consists of reversing the extension mode of SSA so that a retraction plot is also obtained. Hergenrother [*39*] has applied this tensile retraction method for determination of cross-link density of elastomeric polyurethanes.

CONCLUSIONS

A wide range of automated and computer-controlled instruments is available for determination of dynamic mechanical and tensile properties. Careful review of variable features is necessary to insure suitability for property determinations on coating samples of normal thickness. Determination of basic physical properties makes it possible to integrate structure/property knowledge from many polymer fields with coatings research and development. Free film coating data are much more useful when thoughtfully interpreted in relation to results from tests carried out with films intact on their end-use substrates. This review includes many examples that illustrate the benefits of combining DMA or SSA data with results from well controlled and documented tests as provided by the ASTM. The goal of much of the discussion provided here is better understanding of hardness, flexibility, post-formability, solvent resistance, and abrasion resistance.

DMA and SSA are often complementary because strains imposed on test samples are very different. SSA provides information on yield behavior and failure at high strains. DMA provides low strain properties and reveals the viscoelastic nature of coatings very directly and quantitatively.

For unpigmented thermoset coatings, values of storage modulus, E', in the rubbery plateau can be used to calculate cross-link density (XLD). Determination of XLD usually makes it possible to confirm or deny that purposeful reformulation or changes in resin structure have had the desired effects.

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47

Flexibility and Toughness*

by Mark P. Morse[1]

DEFINITIONS

TO PERFORM PROPERLY IN USE, a coating must possess the proper amount of flexibility and toughness to withstand cracking when subjected to stresses produced by shrinking or swelling, forming, mechanical abuse, and weathering. Flexibility is the ability of a material to be bent or flexed without cracking or undergoing other failure. Toughness is the strength and resilience of a material; it is the material's ability to withstand great strain imposed in a short time period without tearing, breaking, or rupture.

INTERPRETATION

The flexibility of a coating applied to a substrate depends not only on its distensibility, but also on the coating thickness and on the adhesion between coating and substrate. Good adhesion tends to give better apparent flexibility than does poor adhesion. The toughness of a coating is dependent on its hardness, stiffness, resiliency, distensibility, and the existence of an energy dissipation mechanism that operates at temperatures far below room temperature and is discernable by dynamic mechanical measurements made over a broad temperature or frequency range.

Generally, the bend and impact tests used to evaluate flexibility and toughness are much more severe than actual service conditions. This is because the tests are usually performed on relatively fresh, unaged coating films. Since coating films tend to lose flexibility during use due to volatilization of free plasticizing components and chemical changes such as degradation, cross-linking, and the like, these severe tests that exceed normal expectations are useful in predicting long-term serviceability [*1*].

BASIC PROPERTIES AFFECTING COATING PERFORMANCE

Both flexibility and toughness depend on very basic properties: the viscoelastic behavior of the coating and its physical transitions and relaxations. The following is a discussion of these properties taken from a paper by Skrovanek and Schoff [*2*].

Coatings, as the polymers from which they are prepared, are viscoelastic in nature, that is, they behave both as viscous liquids and as elastic solids. The coatings have elastic recovery and yet will flow with time when placed under a stress. In general, viscoelastic behavior and mechanical properties are markedly affected when a coating enters the glass transition, softening point, or other relaxation. To be certain that the properties of a coating will fulfill the needs of its intended use, the viscoelastic behavior of the coating should be measured, controlled, and designed to meet the particular end use.

The softening point of a coating can be used as an index of flexibility. The softening point is between the temperature where the coating changes from being hard and glassy and the temperature where it is leathery or rubbery. For example, if a coating has a softening temperature region near the temperature of the forming operation, the coating is less susceptible to failure by cracking or a similar mechanism than if the softening region was above the forming temperature. Measurement of energy storage (related to elasticity) and energy loss (related to viscous losses) as a function of temperature is a means of predicting impact resistance.

Impact resistance of a paint film can be considered as energy dissipation by vibration or rotation of various molecular segments so that at no time will sufficient energy be focused to cause fracture. Since the impact tests performed on paint films often produce deformations beyond the elastic limit of the films, flow within the films must take place or fracture will occur [*3*].

To obtain good impact resistance, the paint film must consist of a polymer that has a sufficiently high molecular weight to have strong intermolecular entanglement (and therefore, high tensile strength), but sufficiently low viscosity (by choice of proper molecular constituents and limiting molecular weight) that flow and accompanying energy dissipation will take place.

Polymer viscosity increases as molecular weight increases so that polymers with very high molecular weights will have greater flexibility than those polymers with intermediate or low molecular weights. At the same time, molecular weights below the critical molecular weight for entanglement lead to very low tensile strengths and the mechanical behavior observed is brittleness. It has been found that modulus is the dominant factor in the relationship between the tensile properties of a coating and its impact resistance [*4*].

In addition to dynamic mechanical behavior, the relaxation behavior as measured by dissipation or damping of coatings has been determined by application of dynamic electrical tests [*5*]. In a dielectric relaxation test, a periodic electrical

*This chpater is an abridged and modified version of the chapter entitled "Flexibility," written by Garmond G. Schurr, found in the previous edition of this manual.

[1]Consultant, 71 S. Shelburne Rd., Springfield, PA 19064.

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potential is applied to the sample coating situated between a pair of electrodes. The dielectric constant and dissipation factor are measured as a function of frequency and temperature.

TECHNIQUES FOR MEASURING BASIC VISCOELASTIC PROPERTIES

Thermal Mechanical Analyzer (TMA)

This instrument employs transducers to sense the position of a vertical rod that rests on the surface of a coating sample. The instrument is usually equipped with a furnace and program planner so that heating, cooling, and isothermal temperature operations can be employed.

With its use, softening points and glass transitions can be determined from plots of coating indentation as a function of temperature. Also, changes in stresses within a coating at a constant temperature (creep) can be determined from plots of indentation versus time [*2*].

Dynamic Mechanical Thermal Analyzer (DMTA)

This instrument produces vibrations in a coating film over a wide frequency range and/or temperature range. It can scan a wide range of sample temperatures at different rates. The resulting deformations from the sinusoidally applied stresses are analyzed to compute values related to energy storage and energy loss [*2*].

EXTERNAL FACTORS AFFECTING FLEXIBILITY AND TOUGHNESS

Flexibility and toughness are not constant characteristics of a specific coating. A number of external factors affect these properties.

Humidity

Water is a good plasticizer for almost all paint films. A change in relative humidity of as little as 2% can be detected in flexibility measurements. Some paint films, such as those based on latexes, imbibe moisture very rapidly, whereas others reach equilibrium with the atmosphere very slowly. It is imperative that tests be conducted in an atmosphere of controlled relative humidity and that the specimens are conditioned in that atmosphere for a day or more before the tests are performed. Generally, flexibility and toughness tests are carried out at a relative humidity of 50 ± 5%. The 10% tolerance is needed because of the difficulty in more accurately controlling relative humidity in most laboratories. If the environment cannot be controlled at this recommended level, then the relative humidity should be measured and reported along with the mechanical properties.

Temperature

The flexibility and toughness of coatings are dependent on temperature. This is particularly true of thermoplastic coatings, but it also is a factor for thermoset coatings. These coatings have a definite second order transition temperature known as the glass transition temperature, T_g. Coatings at a temperature below T_g are hard and brittle with poor flexibility and impact resistance unless there is another relaxation at low temperatures as exists in polycarbonates that have a high T_g of about 160°C (at 1 Hz) and yet have excellent impact resistance because of a relaxation that occurs at about −90°C (at 1 Hz). If coatings do not have this type loss mechanism, at temperatures just above T_g they are flexible, and at temperatures substantially above T_g they tend to develop viscous rather than elastic properties. There is a tendency for all thermoplastic coatings to have identical flexibility properties if these properties are measured at the same temperature relative to T_g, for example, at 10°C above T_g [*1,6*].

Flexibility and toughness measurements are usually made at a temperature of 25 ± 1°C after the coatings are equilibrated at that temperature. However, there are many instances when test are performed at lower temperatures as might be encountered in cold climates.

Strain Rate

Strain rate is the rate at which a coating specimen is elongated and is usually expressed in percent per minute, in./in./min or cm/cm/min. This is the rate of extension relative to specimen size. That is, if a specimen 10 cm long is elongated at rate of 1 cm/min, it is the same as a specimen 1 cm long being elongated at a rate of 0.1 cm/min (1 mm/min). In both cases, the strain rate is 10% per minute.

Strain rate has a great influence on the flexibility and toughness of a coating. In general, the effect of increasing the strain rate is similar to decreasing the coating temperature, that is, as the strain rate is increased, flexibility and toughness decrease.

There can be critical strain rates where flexibility has sharp changes which are very similar to the effects produced at the glass transition temperature [*7*]. This means that the strain rate used in a test must be closely controlled. In some tests, such as bend test, this is difficult to do. This also means that tests performed at a low strain rate (cupping test) are likely to produce different flexibility ratings than those produced by a high strain rate (conical mandrel test) [*1,7*].

FLEXIBILITY AND TOUGHNESS MEASUREMENTS

Mandrel Bend Tests

Both conical and cylindrical mandrels are often used for evaluating the flexibility of coatings. Even though it is difficult to control the strain rate in these manually operated tests, they can provide very useful flexibility ratings.

Conical Mandrel Tests

A conical mandrel test consists of manually bending a coated metal panel over a cone. As described in ASTM Test Method for Elongation of Attached Organic Coatings with Conical Mandrel Apparatus (D 522), a conical mandrel tester consists of a metal cone, a rotating panel bending arm, and panel clamps. These items are all mounted on a metal base as

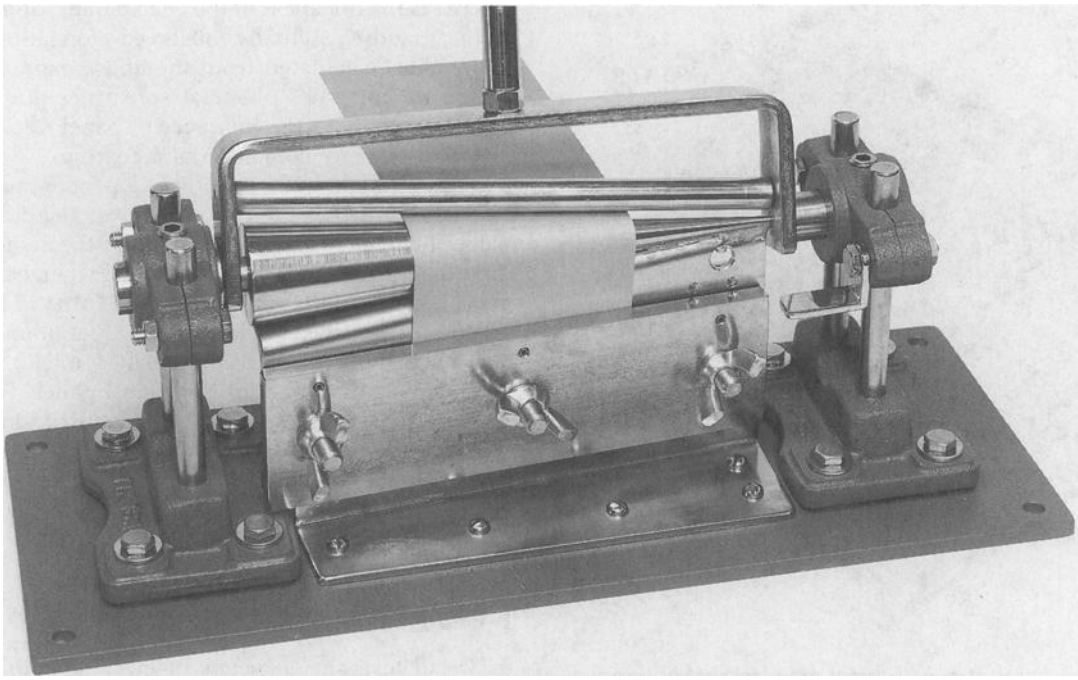


FIG. 1–Bending a specimen over a conical mandrel (courtesy of Gardner Laboratory) [*1*].

illustrated in Fig. 1. The cone is smooth steel 8 in. (203 mm) in length with a diameter of ⅛ in. (3 mm) at one end and a diameter of 1.5 in. (38 mm) at the other end.

When a coating is applied on a 1/32-in. (0.8 mm)-thick cold-rolled steel panel, as specified in ASTM D 522, a bend over the mandrel produces an elongation of 3% at the large end of the cone and of 30% at the small end of the cone. The coated panel is bent 135° around the cone in approximately 1 s to obtain a crack resistance rating under simulated abuse conditions. In some instances, longer bend times have been found to be useful. For example, if the percent elongation of the coating at the point of cracking is to be determined, the method specifies a bend time of 15 s.

Since variations in temperature and humidity can affect mandrel bend tests, it is imperative that the coated panels be conditioned at a standard temperature and relative humidity before performing the test, which is conducted under the same conditions.

The crack resistance value of a coating is obtained by measuring the distance from the furthest end of the crack to the small end of the mandrel. This distance is converted to cone diameter by means of a plot given in ASTM D 522. The mandrel diameter at which cracking occurs is taken as the crack resistance value.

If the elongation of the coating at the onset of cracking is to be reported, a bend time of 15 s is used and the diameter at which the onset of cracking occurred is converted to percent elongation from a plot given in ASTM Test Methods for Mandrel Bend Test of Attached Organic Coatings (D 522).

Cylindrical Mandrel Bend Tests

When executing cylindrical mandrel flexibility tests, a coated panel is bent manually over one or more cylindrical rods or surfaces of different diameters. ASTM D 522 states that the testing device should include mandrels with 1-in. (25 mm), ¾-in. (19 mm), ½-in. (12.7 mm), ⅜-in. (9.5 mm), ¼-in. (6.4 mm), and ⅛-in. (3.2 mm) diameters. Examples of cylindrical mandrel testers are given in Figs. 2 and 3.

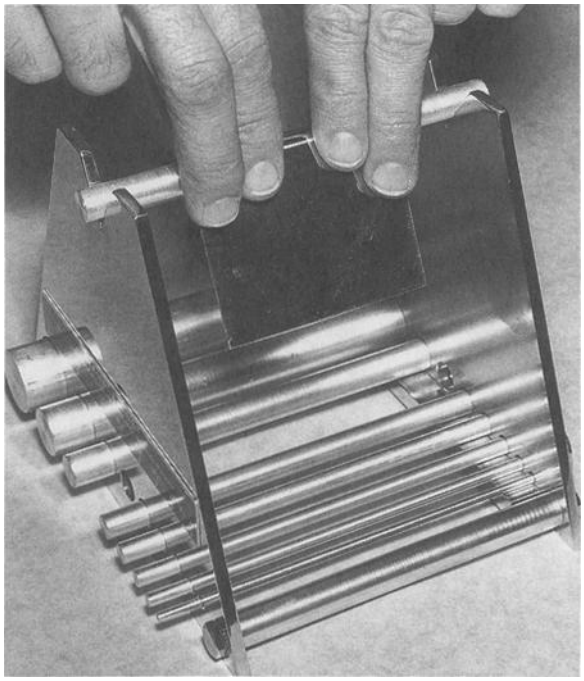


FIG. 2–Bending a specimen over a cylindrical mandrel (courtesy of Gardner Laboratory) [*1*].

The panel should be bent over a mandrel with the uncoated side of the panel in contact with the mandrel surface. The panel should be bent approximately 180° around the mandrel at a uniform velocity in a time of 1 s. If cracking has not occurred, the procedure is repeated using successively

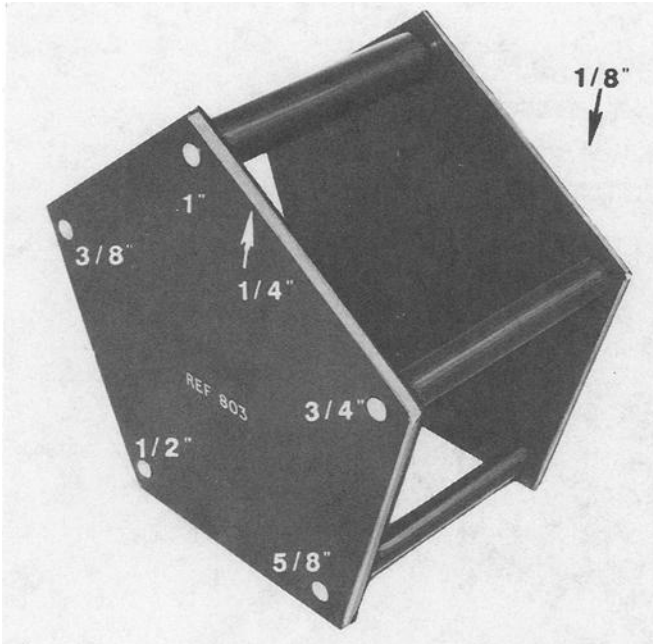


FIG. 3–An illustration of a cylindrical mandrel test apparatus.

smaller and smaller diameter mandrels until cracking is apparent. The cracking-resistance value of a coated panel is the minimum diameter at which cracking does not appear.

This testing procedure can be applied as a "pass/fail" test by determining whether cracking is produced by bending over a specified mandrel diameter.

A table for converting mandrel diameter to percent elongation is given in ASTM D 522. The relationship between diameter of a mandrel and the elongation of a coating has been derived by Schuh and Theuerer [*8*] to be:

$$\text{Percent Elongation} = 100(t/(2r + t)) \qquad (1)$$

where t is the thickness of the coated panel and r is the radius of the mandrel. Actually, observed elongations are greater than values calculated from the above expression and vary with different types of metal substrates. Table 1 contains information about the influence of panel thickness and type metal on percent elongation of a coating.

Crack resistance of a coating is dependent on its thickness, that is, the thicker the film, the lower the crack resistance. Values of crack resistance obtained by the mandrel bend tests should be corrected for film thickness when comparisons are made between different coatings. ASTM D 522 contains corrections to be added to elongation values obtained with coatings having thickness greater than 1 mil (0.03 mm) when applied to ⅛-in. (0.8-mm)-thick steel panels (Table 1).

Conical mandrel bend test procedures similar to those given in ASTM D 522 are found in ISO Method 6860 and BS 3900. Cylindrical mandrel bend test procedures similar to those given in ASTM D 522 are found in ISO 1519, DIN 35 152, and BS 3900 E1.

T-Bend Tests

T-bend tests are a means of evaluating the flexibility of coated strip metal that is to be formed during a fabrication process (Fig. 4). Multiple 180° bends of the coated metal are made, and the amount of cracking produced at each bend is visually determined. Ratings are classified as 0T, 1T, 2T, 3T, and so on. The 0T (pronounced zero T) bend consists of making a 180° bend with the paint on the outside of the bend and pressing the bend flat so there is no space between the metal surfaces. This operation is repeated successively to produce a 1T (pronounced one T), 2T, 3T, etc. bends (Fig. 5). These successive bends result in two, three, etc. thickness of the metal around the first bend. It should be apparent that the greater the number of thicknesses around which the coated metal is bent, the less severe the test. The DiAcro Brake Form machine is suitable for this test.

TABLE 1—Factors affecting elongation measurements of coated panels by mandrel bend tests.

	Mandrel Diameter, in.					
Panel Thickness	1	¾	½	⅜	¼	⅛
CORRECTIONS TO BE ADDED FOR THICKNESS OF PANEL SUBSTRATE						
1/64 in. Correction, %	1.5	2.0	3.0	4.0	5.9	11.1
1/32 in. Correction, %	3.0	4.0	5.0	7.7	11.1	20.0
1/18 in. Correction, %	5.9	7.7	11.1	14.3	20.0	33.3
	Mandrel Diameter, in.					
Metal Type	1	¾	½	⅜	¼	⅛
CORRECTIONS TO BE ADDED FOR TYPE OF METAL PANEL SUBSTRATE						
¾ hard brass Correction, %	3.4	4.6	6.9	9.6	14.2	29.1
Annealed brass Correction, %	3.6	4.9	7.5	10.3	15.9	33.5
Cold-rolled steel Correction, %	3.3	4.4	6.7	9.0	13.8	28.0
	Mandrel Diameter, in.					
Metal Type	1	¾	½	⅜	¼	⅛
CORRECTIONS FOR FILM THICKNESS TO BE ADDED PER MIL OF COATING						
¾ hard brass Correction, %	0.21	0.26	0.38	0.50	0.73	1.38
Annealed brass Correction, %	0.21	0.26	0.38	0.50	0.74	1.43
Cold-rolled steel Correction, %	0.21	0.26	0.38	0.50	0.73	1.37

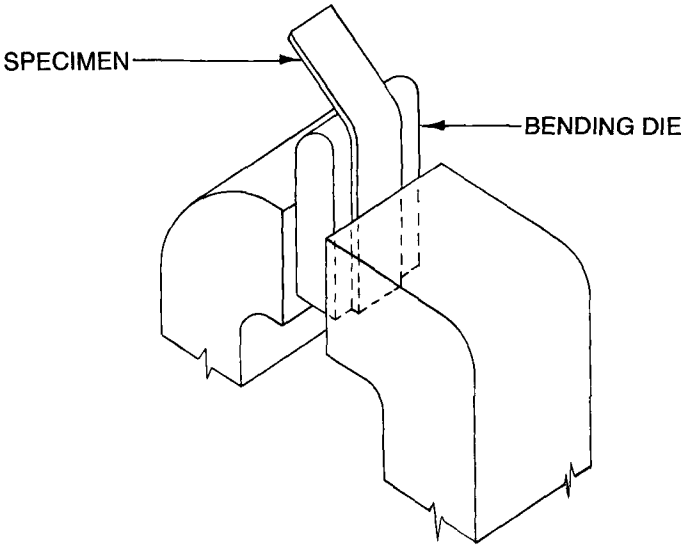


FIG. 4–T-Bend test using a die around which the specimen is bent (ASTM D 4145: Test Method for Coating Flexibility of Prepainted Sheet).

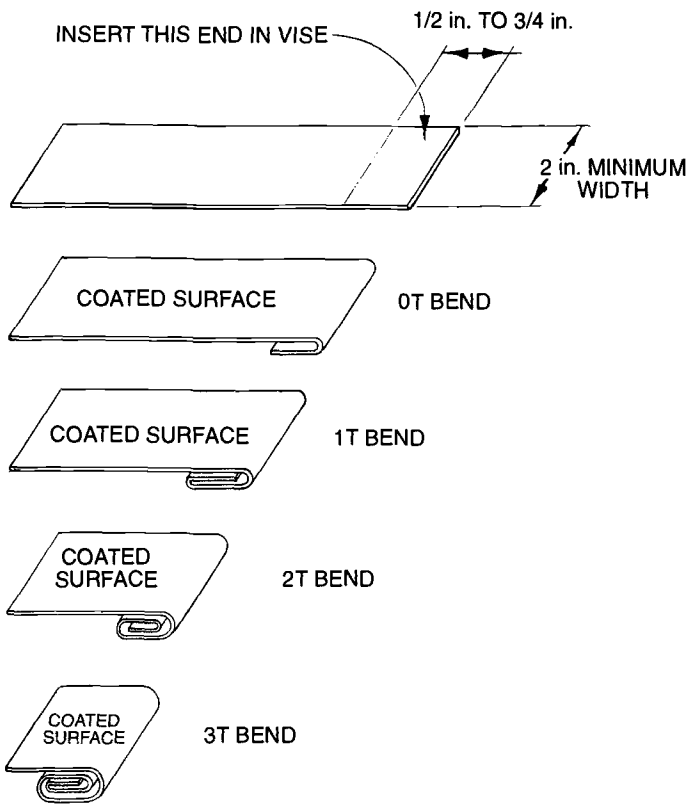
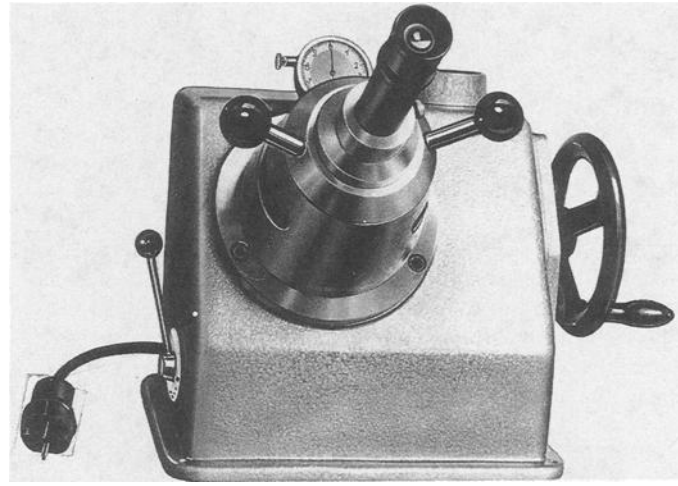


FIG. 5–T-Bend test in which the coated specimen is bent around itself (ASTM D 4145: Test Method for Coating Flexibility of Prepainted Sheet).

Test results are reported as passing the smallest T-bend on which cracks are observed. In some cases, cracking can be detected by removal of a pressure-sensitive tape placed on the bend edges and observing the degree of removed coating particles. ASTM Test Method for Coating Flexibility of Prepainted Sheet (D 4145) describes this test procedure.



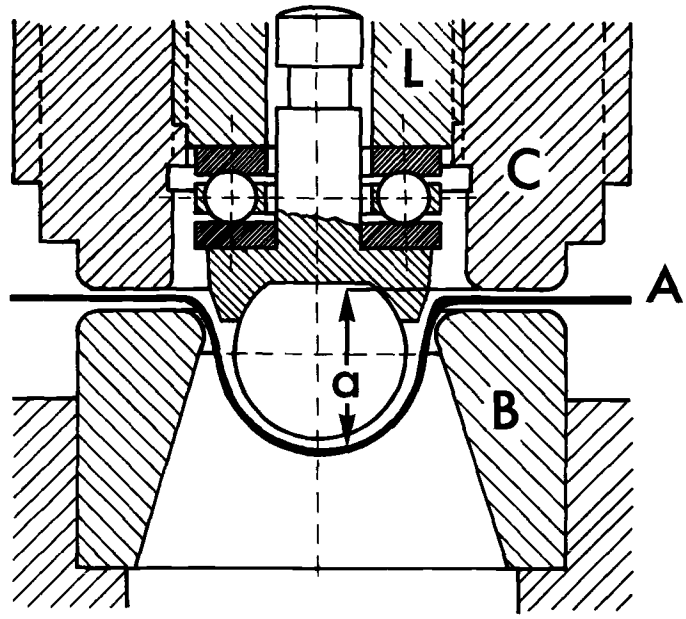


FIG. 6–Erichsen Cupping Tester (early model).

Cupping Tests

A relatively slow rate of forming test can be conducted with a cupping tester that pushes a punch into the unpainted side of a coated panel until the increasing deformation produces cracks in the coating. Test procedures are given in ISO TC 35, BS 3900 E4, NFT 30-019, SIS 18 41 77, DIN 50 101, and DIN 50 102. There are six models of Erichsen Cupping Testers; they provide different test conditions to simulate different forming operations. Two of these models are shown in Figs. 6 and 7. BYK-Gardner Cupping Testers are also suitable for conducting these test procedures (Fig. 8). The BYK-Gardner devices use a spherical punch and provide a range of cupping speeds. The maximum cupping depth is approximately 18 mm (0.7 in.). The cupping action is stopped when cracking in the coating is visually detected. The depth of cupping at that point is indicated on a digital display and is considered to be the flexibility rating. The cupping tester can be equipped with a stereo microscope for observing the onset of cracking.

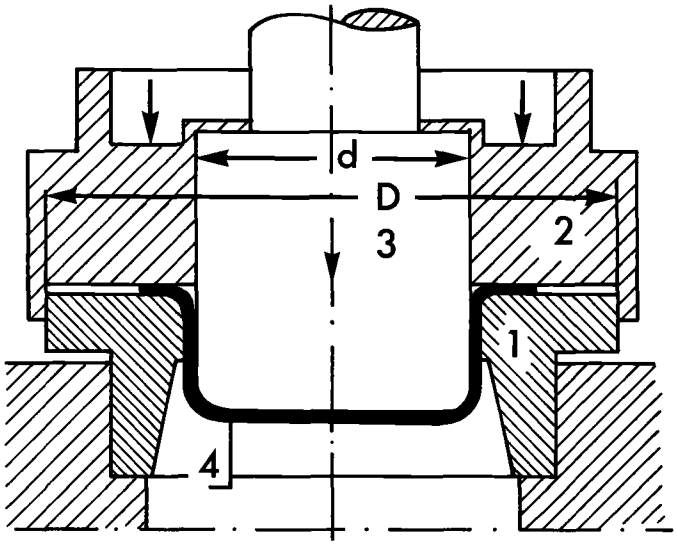


FIG. 7–Erichsen machine for testing stamping lacquers (early model). (Figure from previous edition of this manual.)

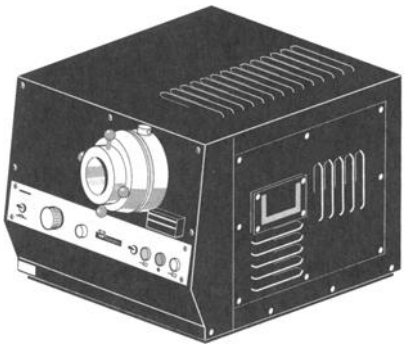


FIG. 8–BYK-Gardner Cupping Tester.

Forming Tests

In many industrial operations, metal is coated flat and then formed into various shapes by drawing the coated metal. This can be simulated directly or by elongating a coated metal sheet. A testing machine that has provided useful formability evaluations is the Erichsen Stamping Testing Machine (Fig. 7). It provides deformations in a few seconds by application of high pressure to a stamping tool. The stamped coated metal is examined for cracking as a "pass/fail" test.

Any tension testing instrument capable of rapidly elongating a metal strip can be used for determining drawability. A coated metal strip would be elongated at a high rate of strain until cracking occurs. The elongation would be measured with an extensiometer [*1*]. Drawability would be reported as the percent elongation obtained just before cracking is observed. Since elongation is rate dependent, the rate of elongation used should be reported.

ASTM Test Method for Formability of Attached Organic Coatings with Impact-Wedge Bend Apparatus (D 3281) describes a procedure for determining the formability of coated metal strips using an impact wedge bend apparatus termed the Coverall Bend Tester (Fig. 9). At the start of the test, the coated panel is bent 170 to 180° over a ⅛-in. (3.2 mm) cylindrical mandrel attached to an impact platform. The platform is adjusted to provide a taper of 0 to ⅛-in. This allows the platform to create a wedge that provides stress angles between 170 and 180°. The end of the coated panel with the 180° stress angle is defined as having 0T bend. The height of the impacter is adjusted until the load to produce a 0T bend is determined. The distance of the cracking produced in the coating by the impact is measured from the edge of the most severe bend outward to the edge of the least severe bend. The amount of film removed from the coating is indicative of its lack of formability.

ASTM Test Method for Formability of Zinc-Rich Primer/Chromate Complex Coatings on Steel (D 4146) also provides a procedure for determining the formability of coated strip metal. An outline of a testing machine that can produce a sufficiently high pressure for pressing a 1⅝-in. (41-mm)-diameter indenter ball into the coated metal is provided. The rate of forming can be adjusted over a range of 0.2 to 1.0 in./min (4.8 to 25 mm/min). A dial gage monitors the movement of the indenting ball. Adhesive tape is applied over the dome formed in the metal, and the tape is rapidly removed. The amount of coating removed is given a rating by comparing it with a set of photographic standards.

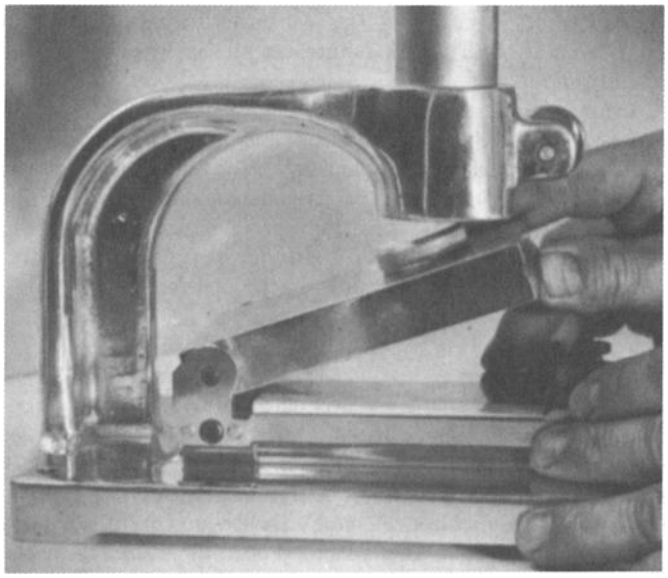


FIG. 9—Coverall bend test. After specimen is bent over a ⅛-in. mandrel, the bent portion is shaped into a wedge when a more severe test is needed (ASTM D 3281: Test Method for Formability of Attached Organic Coatings with Impact-Wedge Bend Apparatus).

Impact Resistance Tests

The most commonly used impact testers drop a weight onto an indenter resting on the surface of a coated panel that is resting on a platform (Fig. 10). A die in an opening in the platform allows the panel to be pushed down by the indenter to form a dimple in the panel. The weight is dropped through a guiding tube whose height is marked in increments.

There are a number of possible combinations of weights, indenter sizes, die sizes, and weight heights that can be used in performing impact tests. The tests can be performed by impacting either the coating directly (coating facing upward) or indirectly (coating facing downward).

Cracking observed on or around the impact-produced dimple is considered failure, and the force to produce the cracking is given in inch-pounds (killigrams-meters), that is, weight times height. The test can be performed either to determine the inch-pounds required to produce cracking or to determine whether a coating passes or fails at a specified inch-pound value. ASTM Test Method for Resistance of Organic Coatings to the Effects of Rapid Deformation (Impact) (D 2794) describes such a test procedure and offers three procedures for determining the degree of cracking produced in an impact deformation: (a) visual inspection with a magnifier, (b) visual inspection after application of an acidified copper sulfate solution, and (c) use of a pin hole detector.

The General Electric Impact Flexibility Tool is used for simultaneously making several indentations of different sizes. From these indentations, conclusions can be made regarding crack resistance and the amount of draw that a coating applied to sheet metal can tolerate. This tester consists of a steel cylinder that has knobs (segments of spheres) of different radii machined on each end. The cylinder is dropped onto a coated panel that is supported coating side down by a rubber pad. The height of drop is adjusted so that the boundary of the cylinder is just discernible. This procedure assures that each knob is used to its limit. Eight knobs cover a range of 0.5 to 60% elongation. See Federal Test Method Standard 141C, Method 6226.

ASTM Test Method for Impact Resistance of Pipeline Coatings (Falling Weight Test) (G 14) describes a test procedure for determining the impact resistance of pipe coatings. A fixed weight of 3.0 lb (1.36 kg) and having a ⅝-in. nose diameter is dropped through a guide tube onto a coated pipe specimen. The height of the weight is adjusted until the minimum height at which cracking appears is attained. A pin hold detector is used to determine the presence of cracks in the impacted pipe. An equation is given for calculating the impact resistance from the weight and its height of drop required to just produce cracking.

A different type of impact tester was developed and is being used at the Bell Laboratories of AT&T (Fig. 11). A coated panel is subjected to repeated glancing blows by a case-hardened steel ball at the end of a short arm that is pivoted to another arm connected to a rotating shaft. During the test, the coated panel is mounted on a platform that moves so that successive blows do not strike the same spot. The energy level of the blows may be held constant, as in a "pass/fail" test, or it

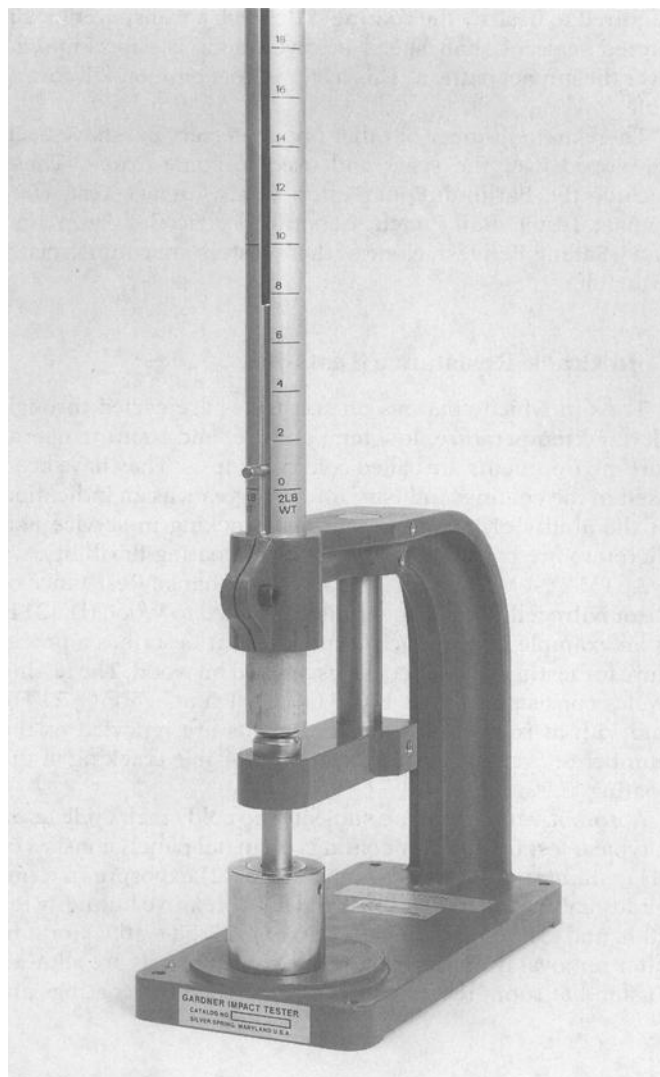


FIG. 10—Gardner impact tester, a falling weight impact tester.

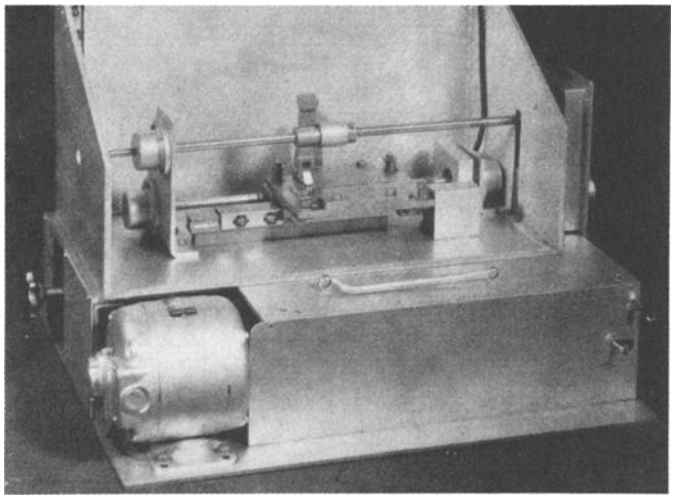


FIG. 11—Bell Laboratories impact tester and specimen. Ball on end of the rotating arm repeatedly strikes specimen, which is moving from left to right (courtesy of Bell Laboratories) [*1*].

can be adjusted by changing the speed of the rotating shaft to determine the onset of cracking. If the hammer energy level required to destroy the coating is desired, a transparent, calibrated scale of shaft speed in revolutions is superimposed over the impact pattern. This tester is not commercially available.

There are a number of other impact testers that have been developed over the years and used to some extent. These include the Parlin-duPont Tester, Camp Impact Test, Hart Impact Tester, Ball Punch, General Electric Ball Drop, and Navy Falling Ball test. None of these testers are commercially available.

Cold Crack Resistance Tests

Tests in which coatings on substrates are cycled through elevated temperature, low temperature, and room temperature environments are called cold crack tests. They have been used in the coatings industry for many years as an indication of the ability of a coating to resist cracking in service and therefore are considered to be tests of coating flexibility.

ASTM Test Method for Temperature-Change Resistance of Clear Nitrocellulose Lacquer Films Applied to Wood (D 1211) is an example of such a cold crack test. It describes a procedure for testing lacquer coatings applied on wood. The testing cycles consists of 1 h at 120°F (49°C), 1 h at −5°F (−21°C), and ½ h at room temperature. Results are reported as the number of cycles required to produce visible cracking in the coating.

Automotive coatings are subjected to cold crack cycle tests. A typical test for exterior coatings on metal panels consists of (1) equilibration at room temperature, (2) exposure in a humidity cabinet at 100°F (38°C) and 100% relative humidity for 20 h, and (3) exposure in a freezer at −22°F (−30°C) for 4 h. After removal from the freezer, the coated panels are allowed to stand at room temperature for 2 h. Then the coatings are visually rated for cracking. In some cases, an exposure of 2 h in an oven at 150°F (65°C) is introduced into the above cycle conditions.

A rapid cold crack test that has been developed is based on the use of cooled air entering a transparent, insulated box. Cold air that has been cooled at a rapid controlled rate is introduced into the box, and the coatings are observed for cracking. The coatings are then rated by determining the temperature decrease from room temperature that is required to produce visual cracks in the coatings [*4*].

Effects of Aging and Weathering

The ultimate measure of satisfactory flexibility and toughness of a coating applied to a substrate is performance under service conditions. Most flexibility and toughness tests are performed on relatively fresh-coated panels, that is, tests are usually performed after the panels have been conditioned in a specified atmosphere for a specified period between 24 h and seven days. The results obtained are applicable to service conditions if these are concerned with post forming or service indoors without a degrading atmosphere, since most coatings do not change appreciably in their physical service properties under such conditions. However, if the service conditions include exposure to weathering, this factor can cause appreciable changes to occur in the coatings properties.

The effects of moisture, temperature changes, and exposure to sunlight (ultraviolet wave lengths) encountered in outdoor exposure generally reduce the flexibility and toughness of organic coatings. Therefore, it often is desirable to conduct tests for flexibility and toughness after periods of weathering to determine how a coating will perform under actual weather conditions [*1*].

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Hardness

by Paul R. Guévin, Jr.[1]

PHYSICAL CONCEPTS OF HARDNESS TESTING

HARDNESS IS A TERM HAVING a different meaning to different people. It is resistance to penetration to a metallurgist, resistance to wear to a lubrication engineer, a measure of flow stress to a design engineer, resistance to scratching to a mineralogist, and resistance to cutting to a machinist. While these actions appear to differ greatly in character, they are all related to the plastic flow stress of the material, i.e., Young's Modulus, Y [*1*]. K. Sato wrote an overview paper on the hardness of coating films [*2*] which merits mentioning and reviewing.

Hardness is not a fundamental property of materials but a composite one dependent on the elastic moduli, elastic limit, the hardening produced by "working" a metal, etc. Empirical relationships are used to determine other properties from the easily measured hardness, but all such schemes are of doubtful or limited validity.

Hardness testing can be a very useful tool for studying modern materials, but it is plagued by well-known experimental difficulties. Reasons for the unusual behavior of hardness data at very low loads are explored by Monte Carlo simulation, which will be discussed later. These simulations bear remarkable resemblance to the results of actual hardness experiments. The limit of hardness as load or indentation depth tends to zero, which is shown to depend on experimental error rather than upon intrinsic material properties. The large scatter of hardness data at very low loads is ensured by the accepted definition of hardness. A new definition of hardness is suggested which eliminates much of this scatter and possesses a limit as indentation depth approaches zero. Some simple calculations are used to show the utility of this new approach to hardness testing.

Over the years, many methods and devices have been employed to measure the hardness of organic finishes. P. C. Wheeler, chairman of a technical committee within the Dallas Paint and Varnish Production Club, as it was called then, reported [*3*] the results of a survey of findings concerning how coating hardness is measured. Following this survey, the first meeting of what is now called ASTM Task Group D01.23.14, Hardness, Mar and Abrasion Resistance, was held in June 1947. The Hardness Group of Subcommittee XVIII, as they were called at the time, of Committee D-1 was organized in Atlantic City to provide an opportunity for expression of opinions by those present concerning their understandings of concepts that were connoted by hardness as applied to organic coating films.

The consensus was that the subject of hardness is very complex. Several of the characteristics of an organic film are simultaneously judgmentally weighed in order of relative importance to obtain the usual expression of hardness judgment. The same physical characteristics of films were employed, and the weighing importance of the various characteristics chosen is not carried out in the same manner; choices are operator dependent and are based on experience with results in practical use of the material.

At the time of this first meeting in 1947, the purpose of the group was to (1) study the subject of hardness and attempt to define some of the physical properties or attributes of an organic coating which affect hardness, (2) limit the study to the development of procedures for measuring the attributes of film hardness, and (3) further evaluate limitations to smooth films of organic coatings as they are normally applied on a substrate. Switzer [*4*] conducted a survey to determine which methods were being used by the coatings industry to measure hardness. They found that some form of scratching or abrasion was used 84% of the time, pendulum or damping hardness (also referred to as entropy hardness) 56% of the time, and indentation hardness 20% of the time. The percentages total more than 100% because some companies surveyed use more than one procedure to evaluate hardness. In 1991, ASTM Task Group D01.23.14 conducted a similar survey. The study showed pencil hardness to be the most commonly used test method with the Sward-type rocker method the next most widely used [*5*]. The modern trend in industries as a whole has been towards an increasing use of indentation methods.

Scratch Hardness

Scratch hardness is the oldest form of hardness measurement and was probably first developed by mineralogists. Back in 1822, F. Mohs [*6*] evaluated comparative scratch hardness of many materials. Assuming the liquid state to be equivalent to "zero" hardness, he arranged solid materials into ten hardness groups, rating them as follows: talc, 1; gypsum, 2; calcite, 3; fluorite, 4; apatite, 5; orthoclase, 6; quartz, 7; topaz, 8; corundum, 9; diamond, 10. As the system was set up, any material of a given Mohs hardness number could scratch any other material with a lower Mohs hardness, and about 99% of all known materials have hardness ranging from Mohs 1 to 9. However, the Mohs scale, though conve-

[1]President, P. R. Guévin Associates, P.O. Box 811, Westerville, OH 43086-0811.

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nient to apply, is essentially qualitative in nature. The wide variety of hardness test procedures that have been used may be described by the following sections.

As user demands for improved resistance to scratch and hardness increased for applications such as automotive finishes, high-performance coatings were developed and became more widely used. As the primary objective was to improve the surface hardness rather than resistance to deformation of the coating, scratch resistance tests were examined [7]. The coatings industry developed, adapted, or adopted various instruments and test methods, which are described below.

Bierbaum Microcharacter—This instrument, designed by C. H. Bierbaum [*8-12*], has a polished prismatic diamond cube (diamond pyramid) held in an elastic support as a scratching tool. It is a rather elaborate device consisting of a microscope, stage, and diamond tool on a balanced arm. The sharp point is the corner of a cube, one edge of which acts as a leading edge, being inclined to the horizontal surface of the specimen at 35.25°. The lubricated specimen is slowly moved under the point, and the standard load is 3 g. The scratch width w in micrometre is measured under a microscope according to recommendations made by the inventor, and several readings are averaged to give:

$$\text{Bierbaum Microhardness} = \frac{10^4}{w^2} \qquad (1)$$

Bierbaum scratch hardness is the ratio of the load on the diamond, in kilograms, to the square of the scratch width (w), in millimetres. It was marketed in the United States by the American Optical Company primarily for testing the hardness of metals. It had been used on plastics [*13*] but never gained general acceptance for use on organic finishes.

In 1958, ASTM Committee D-20 on Plastics adopted D 1526-58T, Tentative Method of Test for Bierbaum Scratch Hardness of Plastic Materials. Their published [*14*] statement said:

> This method fills a need for a test to determine the relative resistance of a plastic surface to defacement by a sharp abrasive particle as occurs in tableware, optical elements, and similar applications.

When the Bierbaum Microcharacter Hardness Tester wasn't useful any more for ASTM purposes, it was withdrawn in 1964.

Clemen Scratch Hardness Tester—The current instrument, shown in Fig. 1, is marketed by Erichsen GMBH & Co. This device is available in two versions: hand-operated and motor driven. Both determine the scratch resistance of protective surface coatings, such as paint and lacquer finishes, plastic coatings, etc. It consists of a sliding test panel carrier mounted on a base frame. A scratching tool is fixed at the end and a sliding weight in the middle of a counterpoised lever that is supported by two pillars. Operated by means of a dropping and lifting mechanism, the scratching stylus or needle is moved along the test surface during the working stroke, but is lifted for the return traverse.

The weight-loaded blade or ball-shaped carbide tool is applied with a defined force (0 to 20 N) to the specimen, which is moved with constant speed. The scratch hardness is measured by the force necessary to cut through the coating to the substrate. It is operated manually or uses a motorized drive. Suitable scratching tools are: the Clemen scratching stylus, a chisel-shaped tool with a tungsten carbide edge, or a scratching needle according to Danske Elværkers Forening (DEF) 1053, Method 14, which is an inexpensive, ball-shaped, hardened-steel tool easily replaced when worn.

Dantuma Scratch Tester—This device was developed in 1940 by H. Dantuma in the physical laboratory of Sikkens (now Akzo-Sikkens) [*15,16*]. It employs a novel means of increasing the load during travel of the scratching tool across

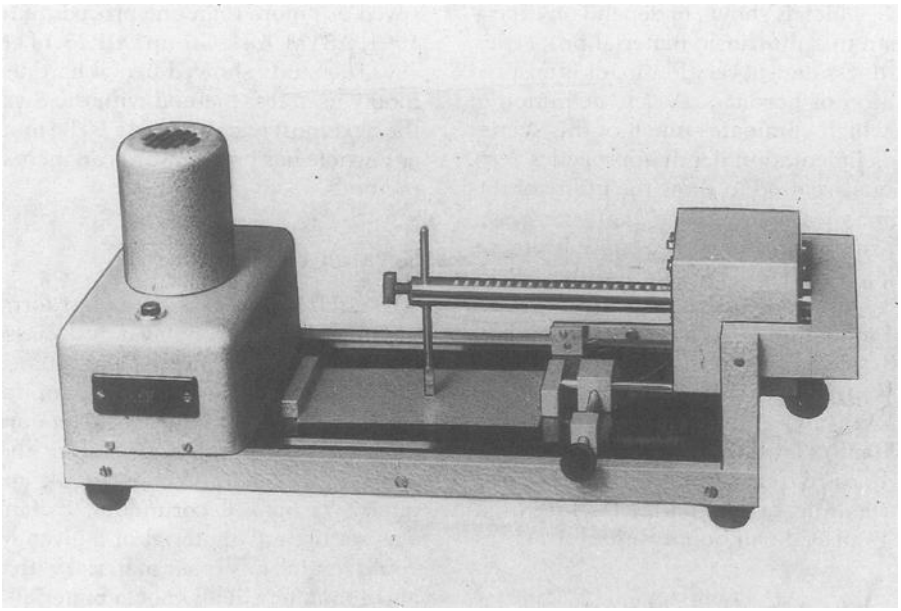

FIG. 1–Clemen Scratch Hardness Tester. (Courtesy of Erichsen GMBH & Co.)

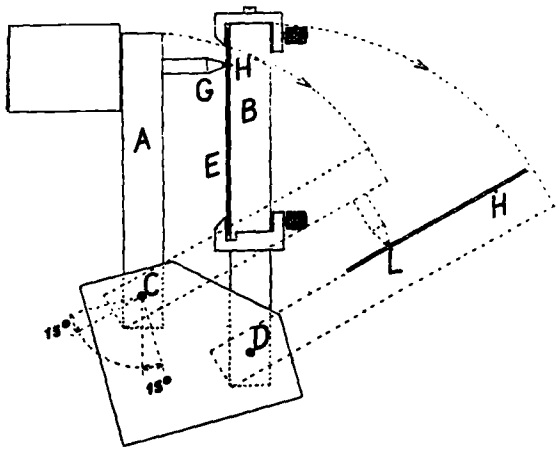

FIG. 2–Dantuma Scratch Tester. (Figure from previous edition of this manual.)

the film. Referring to Fig. 2, as Arm B, with Tool G resting on Panel H, is lowered, Arm A follows. The scratching tool travels from H to L, a distance of 5 cm. The load varies from 0 to 5000 g. Operation may be by hand crank or motor. Four types of hardened-steel scratching tools are provided: a ball 1 mm in diameter, a simulated finger nail, and two wedges. The Dantuma Scratch Tester was never produced for distribution.

du Pont Scratch Testing Machine—This type of instrument was once used at the du Pont lacquer plant at Parlin, New Jersey, for determining the hardness of lacquers and their resistance to scratching. It was one of the first to electrically signal the end point of the test. It is shown in Fig. 3.

The device consists of a wooden base on which is mounted: (1) a fulcrum holding a graduated level equipped with weights and a needle point, (2) a transformer, (3) a 6-V lamp, and (4) a metal plate. These parts are connected in series, the transformer being used to step down ordinary light voltage to that of the small lamp. The metal panel, coated with lacquer, is placed coated side up on the metal plate under the needle. The weight is adjusted, and the panel is drawn along the plate in the direction of the long axis of the instrument. This operation is repeated, each time using an increased weight, until the needle penetrates the film. When this happens, the electric circuit is closed, and the lamp lights.

Erichsen Hardness Tester—The Erichsen Company [*17*] markets a pocket-size hardness tester, Model 318, shown in Fig. 4, that somewhat resembles a mechanical pencil in appearance. It has three tungsten carbide hemispheres or ball points 0.5 mm (Opel), 0.75 mm (Bosch), and 1.0 mm (to relate to International Standardization Organization [ISO] 1518) in diameter that are spring loaded. Holding the instrument upright and placing its point on the test surface, one draws a 5 to 10-mm-long line at a rate of approximately 10 mm/s. The stylus should produce a scratch that is just visible. By locking the slider each time, one can control the applied pressure, which is marked in newtons. Thus, one can gradually approach the correct setting. Three scales are engraved into the pencil for the three pressure ranges: 1.0 to 3 N (accuracy 0.1 N), 2.0 to 10 N (accuracy 0.5 N), and 3.0 to 20 N (accuracy 1.0 N). The hardness is defined as the minimum load or force, in g, on the ball point, that leaves a mark in the surface just visible to the unaided eye [*18*].

Graham-Linton Hardness Tester—This device, illustrated in Fig. 5, might also be considered an adhesion tester. As shown in the figure, it is essentially a small, circular blade upon which pressure is exerted by a coil spring. A scale, graduated in 100-g increments from 0 to 2000 g, indicates the load on the blade.

Hoffman Scratch Tester—The Hoffman Tester is one of the "old line" instruments in the paint industry and comes as close as any instrument to date of being "the paint chemist's educated knife." Figure 6 shows the original instrument that was developed and patented [*19*]. There is a low carriage with a weighted level on one end. The scratching tool is a sharp-edged, hardened-steel cylinder with its axis at an angle of 45° to the plane of the film. This cylinder is attached to the lever arm, and the load is varied by varying the position of the weight on the lever. This instrument has been used for adhesion and mar resistance tests. A General Electric Company test method [*20*] and a federal test method [*21*] specify how the instrument is to be used. Figure 7 shows the refined instrument. The edge of the hardened-steel tool is positioned at 45° with respect to the test surface and can be loaded at any value between 0 and 250 g or 0 and 2500 g. The Hoffman Tester, when used in the lower range of up to 250 g loading, has been used for determining scratch resistance of a surface coating. It has had its greatest application, however, in the high range, up to 2500 g, for cutting completely through the coating to the support surface for measuring such properties such as degree of cure and adhesion.

In use, the desired loading is set on the cutter dial, and the lower edge of the instrument is held against the test surface to

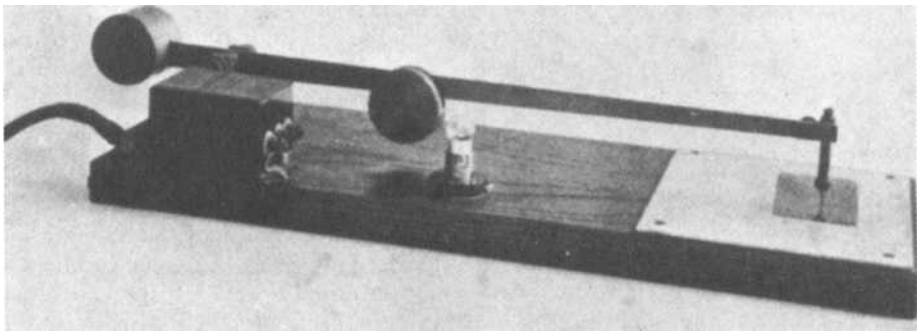

FIG. 3–du Pont Scratch Testing Machine.

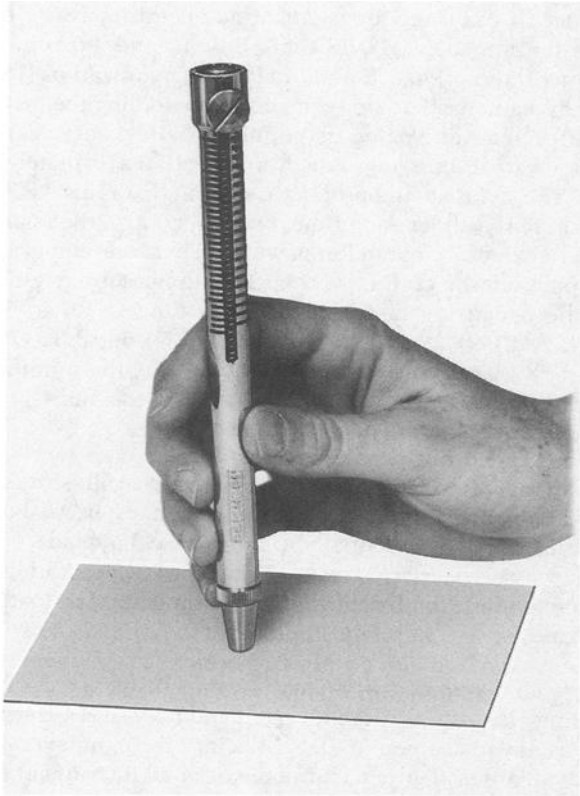

FIG. 4–Erichsen Model 318 Hardness Tester. (Courtesy of Erichsen GMBH & Co.)

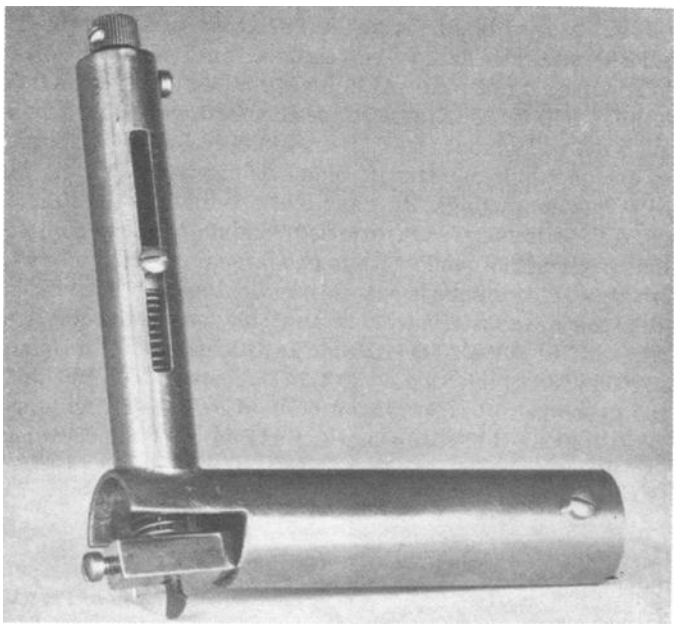

FIG. 5–Graham-Linton Hardness Tester.

ensure uniform contact. While held in this position, the instrument is drawn in a direction away from the cutter. The nature of the mark left by the cutter, if any, is observed, and the test may then be repeated at a different cutter loading.

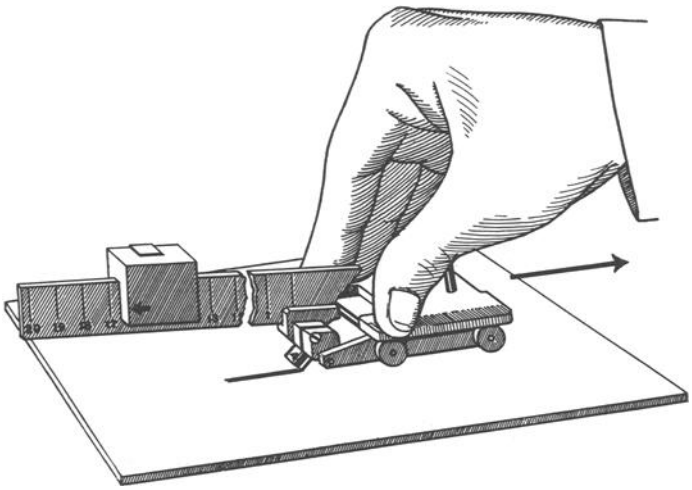

FIG. 6–Original Hoffman Scratch Tester.

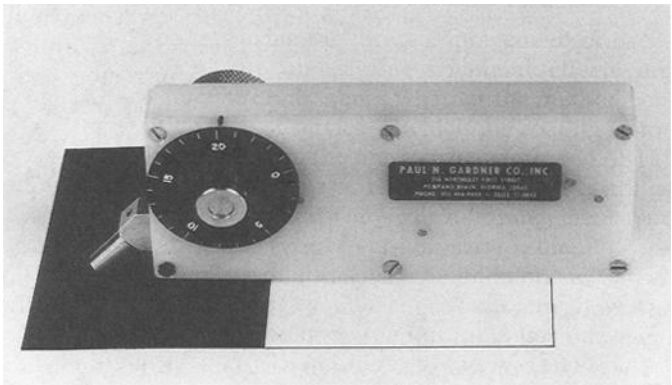

FIG. 7–Current Hoffman Scratch Tester. (Courtesy of The Paul N. Gardner Company, Inc.)

Inspector's Dur-O-Test Pocket Size Hardness Tester—The Inspector's Dur-O-Test Pocket Size Hardness Tester, shown in Fig. 8, is a simple pocket instrument used to evaluate the vulnerability (scratch hardness) of surfaces such as coatings, varnishes, plastic coverings, etc. Especially valuable for quick "on line" tests in plants, paint shops, building sites, etc., it determines the force required to scratch or scar a surface with a defined spherical tool. It consists of an engraving needle with spherical tip of tungsten-carbide of 0.75-mm (0.03-in.) diameter. The spring tension of the tip can be altered and set with a fixing device. The instrument has three interchangeable springs. The limitation is an inability to test elastic coatings.

In the operation, the scratch needle extends slightly out of the jacket. A line is drawn on the surface to be tested in 1 s while maintaining sufficient pressure to keep the needle against the rod stop. If the tension is high, the surface will be clearly marked. If low, there will be no mark. The correct tension will result in a barely visible mark.

Laurie-Baily Hardness Tester—This apparatus [*22*], shown in Fig. 9, was among the first to be developed for films and was invented by A. P. Laurie and F. G. Baily of Heriot-Watt College, Edinburgh. The apparatus consists essentially of a hardened, blunt steel point upon which pressure is exerted by

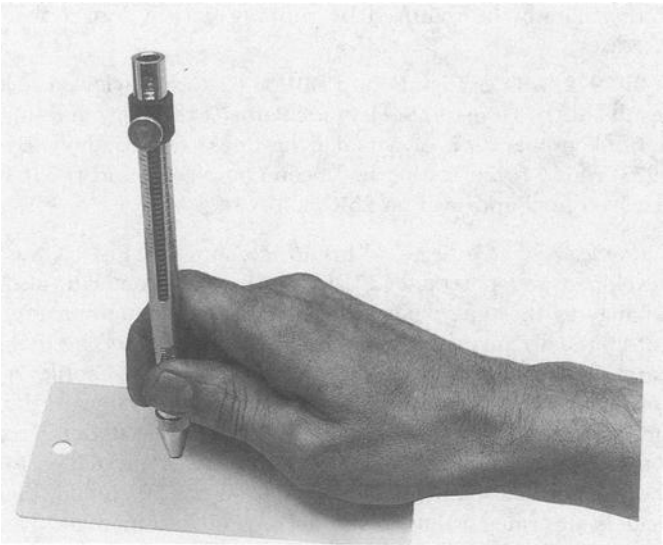

FIG. 8–Inspector's Dur-O-Test Pocket Size Hardness Tester. (Courtesy of The Paul N. Gardner Company, Inc.)

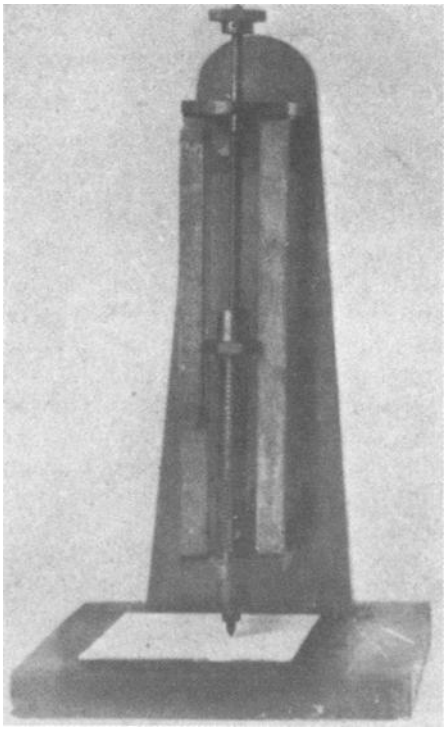

FIG. 9–Laurie-Bailey Hardness Tester.

a vertical coil spring. The spring tension is controlled by an adjusting screw and can vary from 0 to 2000 g. The finish to be tested is placed under the point and slowly moved horizontally by hand as the pressure is increased until a scratch is made. Then the scale readings are recorded.

Parker-Siddle Scratch Tester—This tester is a very simple form of the Schopper type in which the load on a needle is increased as the scratch is made. The point of the needle is a hemisphere 0.2 mm in diameter. The panel carrier is moved by hand, the speed recommended by Parker and Siddle being 30 cm/min. Appreciably greater speeds give inconsistent results.

Pencil Hardness Tester—Rating the hardness of an organic finish according to the hardness of a lead (graphite) pencil that will just scratch it was described by Wilkinson [*23*]. Gardner [*24*] studied the method using pencils sharpened to different shapes: sharp cones, rounded cones, and chisels. He found the principal source of error lay in the character of the point because it was difficult to reproduce points. Other sources of error were the pressure on the pencil and the angle at which the pencil was held while it was moved over the organic finish. Gardner built a device to hold eight pencils at one time at an angle of 45° to the panel, but found that it was impossible to align all pencils uniformly. Modern production has overcome this problem, and several companies offer a pencil hardness gage composed of eight mechanical drawing lead holders (pencils) permanently mounted in a circular array on a plastic cylinder. A small metal tube through the center of the cylinder provides storage for spare leads and a guide for positioning pencils for a test.

ASTM Test Method for Film Hardness Test (D 3363) is practical for laboratory use, for use on a production line, or in the field to assess quantitatively the rigidity or firmness (elastic modulus) of organic coatings applied to rigid substrates such as metal or plastic. Hardness values may define requirements for particular coating applications or may be used to evaluate state of cure or aging of a coating.

In this test, pencil leads of increasing hardness values are forced against a coated surface in a precisely defined manner until one lead mars (marks) the surface. Surface hardness is defined by the hardest pencil grade which fails to mar the organic coating surface.

Today, pencils are available in about 14 different grades of hardness, ranging from the softest, 6B, to the hardest, 6H, although hardnesses greater than 6H have been available. Pencil leads are blends of graphite, clay, and binders. They range in hardness from softest to hardest as follows: 6B, 5B, 4B, 3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H, and 6H. Over the years certain features of the method have been standardized. They are:

1. The lead is "squared" against fine abrasive paper (as opposed to a sharp, fine point).
2. The pencil is held at an angle of 45° to the surface of the test panel.

Variations in the method have occurred with respect to how the test is actually carried out. Smith [*25*] made a study in 1956 and used the following method:

1. Strip the wood from the lead for a distance of approximately ¼ in. (6 mm) using care not to nick the lead. Square the exposed lead by a gentle rotary motion against No. 400 carbide abrasive paper.
2. Hold the pencil in a writing position, that is, at approximately 45° and push forward against the film. Use pressure short of breaking the lead. By turning the pencil after a test, a new edge is available for use, and three or four trials may be made with one dressing of the lead.
3. Clean the marks with a soap or "artgum" eraser. Any marring of the surface, visible at an oblique angle in strong

light, indicates that the pencil is harder than the film. The hardness is expressed as the grade of the next softer pencil.

In developing this method, Smith determined the pencil hardness of 14 different organic finishes that varied widely in hardness. Five different brands of pencils were used, and the results are shown in Table 1. The results indicated that there were variations in hardness between different brands of pencils and that it was necessary to use only one brand to obtain reproducibility.

Smith also compared the Knoop hardness and Sward rocker hardness versus pencil hardness of the 14 organic finishes. These results, also in Table 1, showed that pencil hardness rated the various organic finishes in the same order of hardness as the two other more elaborate methods. This is interesting because, according to Smith, three widely different mechanisms were involved. They are:

Sward rocker = deformation *within* the elastic limit.
Knoop hardness = deformation *beyond* the elastic limit.
Pencil = deformation beyond the elastic limit and tearing away of material.

Smith's work provided a broad foundation for the pencil hardness test, and many features of his method are used today. It was the exact manner in which the pencil was applied to the test that was never adopted.

Those test methods which have been adopted and are used almost universally were outlined by the Houston Society for Coatings Technology [*26*] in 1966. The Houston Society described two basic methods, which were:

1. *The Disbonding Method* in which the pencil, at an angle of 45°, is pushed into the organic finish. The organic finish is considered to have failed when a pencil removes chips, flakes, scales, or shears the finish from the substrate without breaking the lead of the pencil. This method has also been an adhesion test.
2. *The Indentation Method* consists of using the pencil as an indentation instrument by drawing the point (at an angle of 45°) across the film to produce a continuous indentation. The Houston Society developed a special carriage to hold the pencil and apply a load of 200 g to it while the carriage was being drawn across the test panel. The organic finish is considered to have failed when the pencil leaves an indentation in the film (visible under a ×15 magnifying glass) that cannot be removed by rubbing with a soft rubber eraser.

In 1972, ASTM Task Group D01.53.02 Cure reviewed the results of the Houston Society for Paint Technology and undertook preparation of a pencil hardness test method. By 1973, round-robin testing had been completed, and D 3363 received final approval on 25 Oct. 1974.

Rondeau Scratch Tester—This device, shown in Fig. 10, was developed and patented [*27*] by Herbert F. Rondeau, also belongs to the type where the load on the scratching tool automatically increases as the test is being made. The tool, parabolic in shape, is mounted on the free end of a cantilever spring, one end being moveable in a slot in the frame. At the start of a test, the tool rests on the test surface under zero load. The finish end of the slot is 0.100 in. (2.5 mm) nearer to the test surface than it is at the start. At the finish end, the load is the rated value of the spring. At intermediate distances, the load is proportional to the distance. Three springs are provided, giving loads of 300, 600, and 1200 g at the finish end.

Scheppard-Schmitt Scratch Dynamometer—The principle of this device was employed by Eastman Kodak's S. E. Scheppard and J. J. Schmitt [*28*] in the development of a new scratch hardness instrument. The scratching tool is a hardened steel, 45° tetrahedron.

Measurement of scratch resistance is expressed as the threshold load producing a scratch or by a curve expressing the relation between the load and size (width) of the scratch.

Schopper Hardness Tester—This device [*29*], shown in Fig. 11, was one of the first to provide for automatically increasing the load on the scratching tool while the scratch is being made. Arms extending upward from the panel carrier end in slots above the beam carrying the scratching tool. A roller resting on the beam is guided by the slots. As the panel carrier is drawn along, the roller travels with it, thereby increasing the load on the scratching tool. Provision is made for automatically lifting the load from the specimen at the end of each trip and also for a sidewise displacement of the specimen to provide a new path for repeat tests. The interpretation of results is the same as with other types of scratching devices, that is, according to the character of the mark under a partic-

TABLE 1—Hardness test correlation (Smith).

Panel No.	Knoop Hardness	Sward Hardness	Pencil Brand A	Pencil Brand B	Pencil Brand C	Pencil Brand D	Pencil Brand E
1	3.09	24	5B	6B	5B	6B	4B
2	4.33	28	4B	6B	6B	6B	4B
3	2.77	24	5B	6B	5B	4B	4B
4	2.61	22	3B	4B	5B	4B	3B
5	5.81	38	2B	2B	2B	2B	3B
6	9.23	50	HB	F	HB	HB	HB
7	11.2	25	HB	F	HB	HB	H
8	21.1	58	F	H	H	H	2H
9	17.4	54	F	F	F	H	2H
10	25.7	54	H	H	H	H	2H
11	21.0	60	2H	2H	2H	4H	3H
12	39.1	40	3H	2H	3H	4H	4H
13	34.9	30	6H	5H	5H	5H	6H
14	...	40	8H	9H	7H	7H	9H

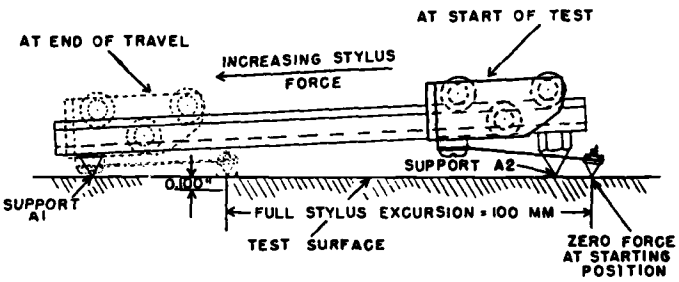

FIG. 10–Rondeau Scratch Tester.

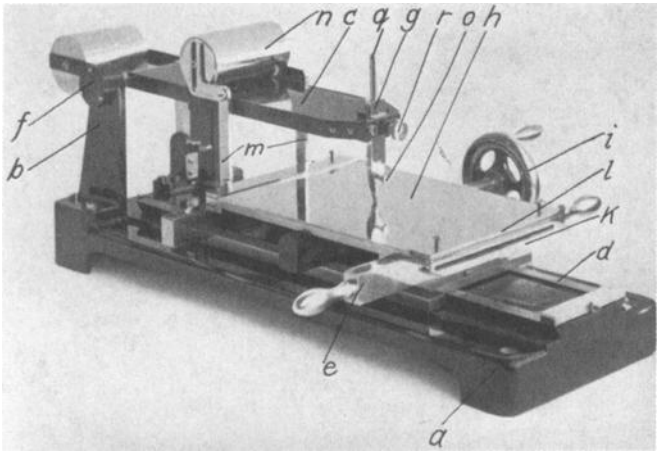

FIG. 11–Schopper Hardness Tester. (Photo from previous edition of this manual.)

ular load or tool, or the load at which a particular tool makes a mark.

Sheen Scratch Tester—This instrument determines the scratch resistance (i.e., scratch hardness) of paint coatings and is designed to meet the requirements of the British Standards (BS) Method of Test for Paints (BS3900: Part E2). Its usefulness, however, extends beyond the rigid limits for operating conditions set by this authority as the test provides data outside the specification. Performance is related to many factors that include the hardness of the coating with other physical properties such as adhesion, lubricity, resilience, etc., as well as the influence of coating thickness and curing conditions. It is a quantitative indication of the extent to which serious damage is resisted when a loaded needle is raked across a relatively smooth, flat surface.

The instrument is shown in Fig. 12. The needle arm is counterpoised and rigid to prevent whip or chatter at the ball point. Weights totaling 2000 g and providing increments of 100 g from 100 g are supplied and additional weights are available. A total load of 6 kg can be used for very hard coatings. A 2000-g weight (or two) is useful for baked coatings. The 1-mm tungsten carbide-tipped needles are held in a chuck and can readily be removed for inspection and replacement.

Sikkens Scratch Hardness Tester—Sikkens Scratch Hardness Tester, Model 601, is marketed by Erichsen Company [*30*] and conforms to ISO 1518, BS 3900: E2 and Stichting Nederlands Normalisatie-Instituut (NEN) 5336. This device simulates a scratching or scouring action and creates stresses under controlled conditions that enable quantitative evaluation of the ability of coatings to withstand repeated horizontal and vertical abrasions. There are three scratching tools: a 1-mm cutting carbide sphere, a Clemen designed scratch cutting tool, and a VW designed scratch cutting tool; two speeds: 35 and 1 mm/s, and two load ranges: 0 to 20 and 0 to 90 N.

The test is performed by selecting a load which is applied to the cutter and can remain either constant in value or automatically increased at a linear rate. The weighted cutter is brought into contact with the coated surface at a constant speed, and it penetrates the coating when a critical force is attained. The force required to be applied to the tool to penetrate the coating and just touch the substrate is the measure at the scratch hardness. Testing using the automatically increased force shortens the test and quickly evaluates the scratch resistance at the coating.

Simmons Scratch Tester—This coating hardness measuring instrument [*31*] is another tester of the increasing load type and is suitable only for films on metal. When the stylus breaks through the film, a relay stops the machine. Hardness is reported as the weight necessary to penetrate the film.

Steel Wool Scratch Tester—The Panelgraphic Rotary Steel Wool Scratch Tester (Fig. 13) is constructed so scratch resistance may be measured using loads of 13 and 24 lb/in.^{2} (0.9 and 1.7 kg/cm^2) on the steel wool pad attached to a square testing foot of 1.25 in.^{2} (8.065 cm^2). The 0000 steel wool on the testing foot is then rotated for five revolutions, after which the sample is visually inspected for scratches in the coating and rated. The test then may be repeated in other locations to determine uniformity of the coating. This instrument is being removed from production and will not be available for purchase.

While this test may be acceptable for materials that are homogeneous or essentially homogeneous, when attempting to measure the scratch resistance of relatively thin coatings, other complicating factors arise. The measured scratch resistance of the coating is dependent upon factors independent of the coating itself, including the coating thickness and the substrate over which the coating is applied. Stated another way, scratch resistance is not an intrinsic property of a coating, and it may mean different things depending on how the property is measured. When attempting to measure only the resistance of a material to surface scratching, the concept of "mar resistance" comes into play.

Teledyne Taber Shear/Scratch Tester—Shear and scratch tests are significant because rigorous controls are exercised over these parameters affecting materials' resistance to shear and scratch. The unique Model 502 Teledyne Taber Shear/Scratch Tester [*32*] features three cutting tools: the S-20 tungsten carbide tool for shear testing and 139-55 and 139-58 diamond tools for scratch testing. The instrument is shown in Fig. 14. A tool is fixed to the underside of a beam pivoted on ball bearings. Riders provide for adjusting the load on the tool between 0 and 1000 g.

The test films for this tester are prepared on panels containing a hole in the middle for locating on a turntable. In making a test, the panel is rotated counterclockwise. Three tools are provided: "thumb-nail" contour shear tool (S-20) lapped to a

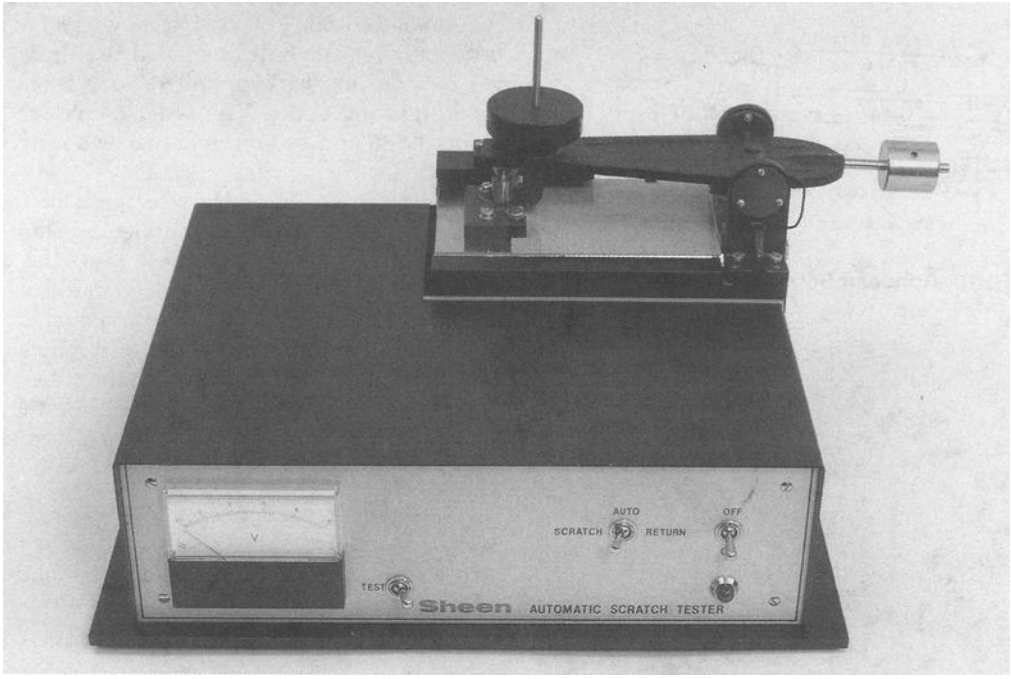

FIG. 12–Sheen Scratch Tester. (Courtesy of The Paul N. Gardner Company, Inc.)

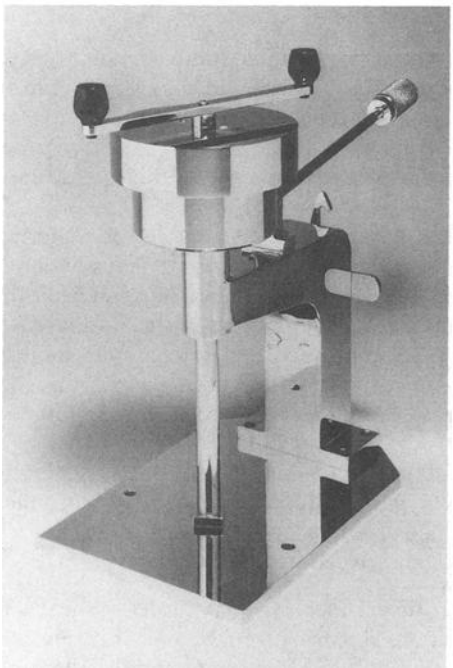

FIG. 13–Steel Wool Scratch Tester. Courtesy of The Paul N. Gardner Company, Inc.)

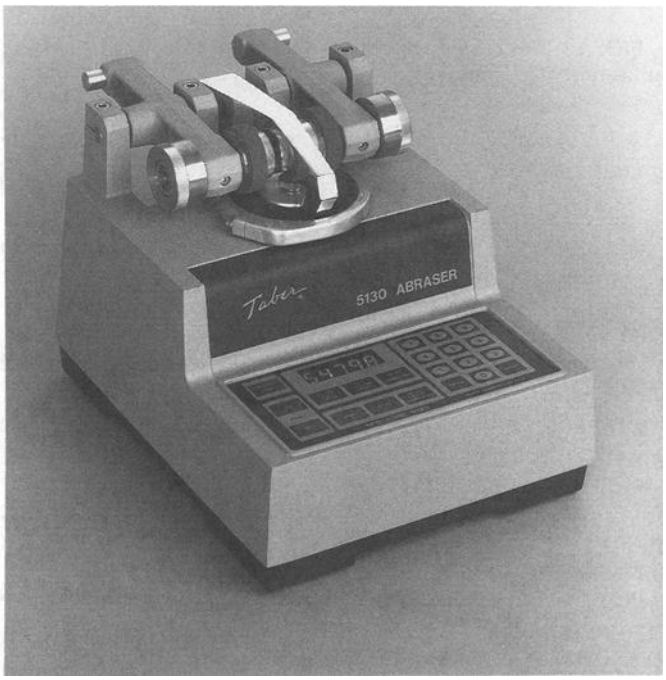

FIG. 14–Teledyne Taber Shear/Scratch Tester. (Courtesy of The Paul N. Gardner Company, Inc.)

25-mm radius with a 30° clearance, a diamond cut to the shape (diamond pyramid) of a corner of a cube, and a diamond cut to the shape of a cone.

Wolff-Wilborn Scratch-Hardness Tester—This test apparatus, shown in Fig. 15, is another pencil method that belongs to the group of scratch-hardness testing instruments that is a simple and quick method for testing the surface hardness of coatings with regard to stresses inflicted by scratching with sharp edges or other rough surfaces. The speed of measuring even permits testing during the production, e.g., coil coating. The test instrument, Model 291, enables the test to be carried out in accordance with Wolff-Wilborn and ensures that the specified force and angle remain constant throughout. This

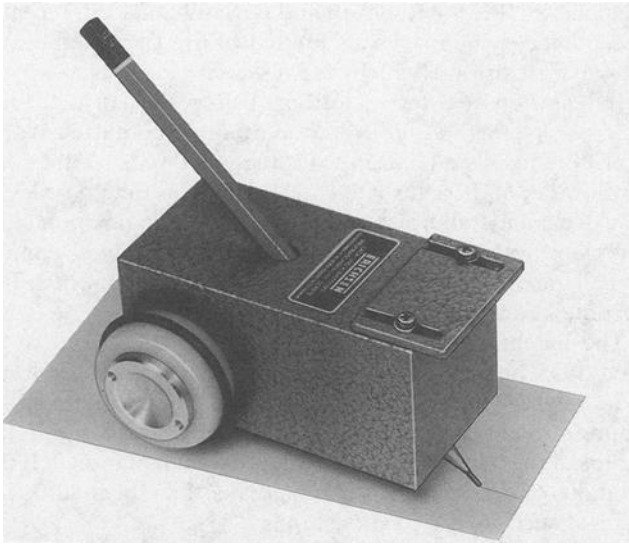

FIG. 15–Wolff-Wilborn Scratch Hardness Tester. (Courtesy of Erichsen GMBH & Co.)

instrument is specified in MIL C 27227, which has been discontinued as a specification.

In the test, pencils of various grades of hardness are moved over the painted surface at an angle of 45° to the horizontal with a 7.5-N (735-dyne) force. The softest pencil hardness that produces injury to the film is the Wolff-Wilborn hardness of the coating.

Universal Hardness and Adhesion Test Instrument—This Erichsen Model 413 hardness tester, shown in Fig. 16, will allow an operator to determine Clemen Scratch Hardness, Micro Scratch Hardness (mar resistance), and the Buchholz Indentation Hardness test Deutsches Institut für Normung e. V. (DIN 53 153) [*33*]. Like its name implies, it is a universal hardness tester.

Indentation Hardness

Microhardness testing has proved to be very popular in many industries because of its simplicity and nondestructive nature. It has been particularly successful for quality control work where it can be used as an indicator of surface durability and, in some cases, of strength. Static indentation hardness tests are "nondestructive" physical tests that employ either a ball, cone, or pyramid that is forced into a surface. The load per unit area of impression is taken as the measure of hardness. The testers use indentors classified by the following names: Brinell, Rockwell, Vickers, and Knoop. A sketch of these indenters is shown in Fig. 17.

The hardness of a material can be defined as a measure of its resistance to indentation. Basically, an indentation hardness test can be classified into two categories [*34*]:

1. Those based on a measure of the residual deformation after the indenter was removed.
2. Those based on the load-indentation characteristics.

Indention hardness values have been reported in a number of different ways, such as: depth of the indentation, the width of the indent, the load necessary to produce a specific depth or length of indent, the load divided by the projected, planar area of indent, etc. The load divided by the projected, planar area of indent is really an expression of pressure and has become the widely accepted method of reporting indentation hardness.

Consider the force on an annulus of radius x and the width dS. The load L is distributed over the contact area as a pressure P. The area of the annulus lying on the curved surface of the indentation is $2\pi x dS$, and the force on it is $P2\pi x dS$ and can be resolved into two component vectors, dH and dV. By conditions of symmetry, the horizontal component dH is an-

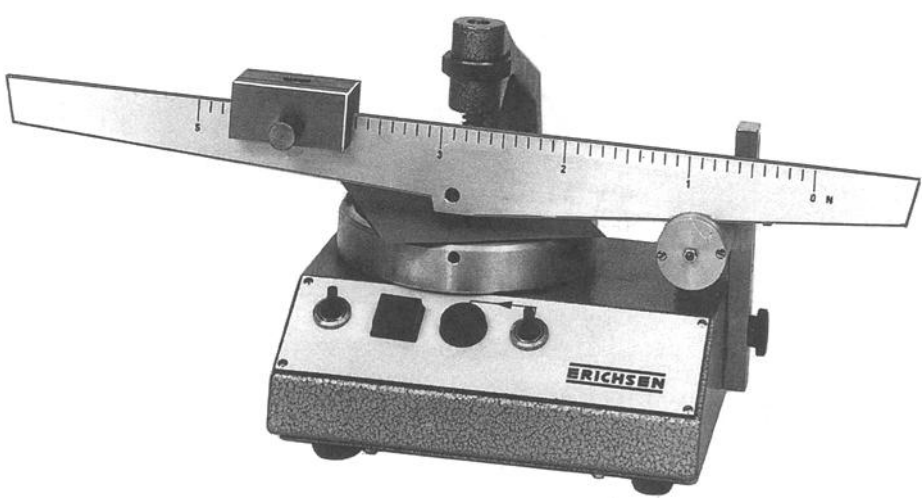

FIG. 16–Universal Hardness and Adhesion Test Instrument. (Courtesy of Erichsen GMBH & Co.)

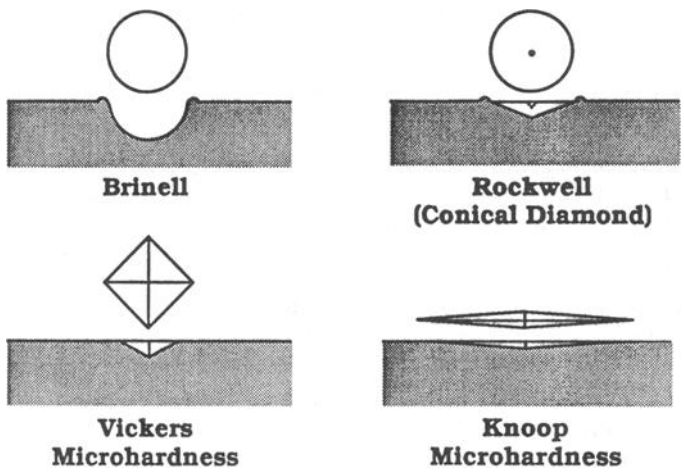

FIG. 17–Hardness indenters' geometries and indentation shapes. (Courtesy of Wilson Instruments, Inc.)

nihilated by an equal and opposite dH on the opposite side of the annulus. The vertical component dV is therefore $P2\pi x dS$ and

$$L = P\pi\frac{d^2}{4} \tag{2}$$

$$P = \frac{4L}{\pi d^2} = \frac{L}{A_p} \tag{3}$$

where P is the mean pressure and A_p is the projected, planar area of indent. Therefore, the mean pressure on the surface of the indenter is equal to the ratio of the load L to A_p.

The indentation hardness tests are performed by pressing an indenter of prescribed geometry against the test surface. The load is controlled at some constant value, and the duration of the indentation process is usually specified for a viscoelastic material. The size of the indentation may be measured with a microscope after the removal of the load. An alternate procedure is to measure the depth of indentation after a given time interval. The latter procedure is preferred for viscoelastic bodies. The hardness number is generally calculated by dividing the load by the area of the indentation. The hardness values obtained are independent of the specimen thickness if the indentation depth is less than one tenth the sample thickness.

Since coating films are very thin, the indentation apparatus must be capable of measuring precisely very small indentations. Because it is difficult to set the zero position, a small preload may be applied before the application of the main load. A number of different instruments, described later, have been devised for making indentation hardness measurements on organic coatings.

The beginning of the twentieth century marked a milestone in the history of hardness testing. In 1900, Dr. J. Brinell, chief engineer at Fagersta Iron Works in Sweden, presented a paper to the Swedish Society of Technologists in which he described his ball test. In the same year, he showed his hardness tester at the Paris Exposition. Following the Brinell innovation was the development of the scleroscope (1906) [*35*]. The 136° diamond pyramid hardness indenter, commonly referred to as the Vickers indenter, was introduced in England in 1925 by R. Smith and G. Sandland [*36*]. Its early acceptance by industry was limited to the largest laboratories, and its use was chiefly for research purposes.

Indentation hardness testing using the Brinell and Scleroscope methods grew in importance, and during World War I practically all hardness testing was done on either one or the other of these instruments. During this time, Stanley P. Rockwell, a metallurgist in a large ball-bearing manufacturing plant, was particularly concerned with hardness control of ball races. As a result, he invented the tester which has become known as the Rockwell Hardness Tester.

The indentation hardness of a material is related to its modulus. The theory of the indentation hardness of an elastic material test has been derived for a spherical indenter. Young's modulus E is related to the indenting force F, the radius of the indenter r, and the depth of indentation h. If the modulus of the indenter is much greater than the modulus of the test surface, the relationship is

$$E = (3/4)(1 - \nu^2)r^{-1/2}h^{-2/3}F \tag{4}$$

where ν is Poisson's ratio (lateral contraction versus longitudinal extension). In the case of viscoelastic materials, a similar relationship holds, but the variation with indenter radius and penetration are somewhat modified. Mercurio [*37*] has discussed the relationship of Tukon hardness to modulus.

The theory of indentation hardness tests on homogeneous materials has received much interest in the last few decades. D. Tabor has been working intensely in this area. In his recent paper [*38*] he said

> The hardness of a solid is usually understood to mean its resistance to local deformation. The simplest method of quantifying it is to press a hard indenter of specific geometry into the body, divide the load by the area of the indention formed, and express the answer in units of kilograms per square millimeters or pascals (1 kg mm^{-2} $\simeq 10^7$ Pa). . . . For elastic solids such as rubber, the indentation pressure is a direct measure of the elastic properties of the material.

Another example of this type study is that of Lebouvier et al. [*39*].

W. W. Walker [*40*] evaluated the Knoop hardness of three organic coatings using a Model LR Tukon Microhardness Tester in accordance with ASTM Test Methods for Indentation Hardness of Organic Coatings (D 1474) except he calibrated the instrument at 100 g load and ran the tests at 200 g load. In addition, he tested the pencil hardness of the same coatings in accordance with ASTM Test Method D 3363. Comparative data are shown in Table 2.

W. W. Walker concluded that a useful correlation existed between the 200-g Knoop indentation hardness and pencil

TABLE 2—Comparison of pencil and Knoop hardness of selected coatings.

Paint	Pencil Lead No.	Lead Hardness, KHN	Paint Hardness, KHN	Difference
Epoxy powder	5H	51.5	30.2	21.3
Polyurethane	3H	45.3	22.7	22.6
Solvent Epoxy	H	31.7	8.9	22.8
Metal Panel	...	...	195 ± 1	...

hardness of thick paint films but that further work needs to be done.

Krautkrämer Branson conducted a similar test using their MicroDur Portable Hardness Tester fitted with a Vickers indenter. The preliminary results, shown in Fig. 18, represent an evaluation of eight organic coatings. The results are promising. However, additional work is needed.

Bell Telephone Laboratories Indenting Rheometer—The BTL Indenting Rheometer, shown in Fig. 19, was designed and developed by Eugene M. Corcoran of the Bell Telephone Laboratories specifically for use as an indenting rheometer, sensitive enough for use with organic coatings but with sufficient load-deflection capacity to make it useful for relatively thick materials such as molded plastics and casting resins.

To achieve this, two separate head assemblies were required. Basically the rheometer consists of a specimen stage or platform, indenter-LVDT transducer head assembly, weights, transducer amplifier indicator, and a 10-in. (25.4 cm) strip chart recorder. In normal use, the specimen or test panel is clamped on the platform, and the instrument is zeroed in with the indent or tip just touching the specimen. This is done by using the knurled rings on the heads and the platform ring (the rings on the sensitive head have 80 threads per inch or 80 threads/25.4 mm) to obtain a coarse adjustment follow by a fine adjustment on the transducer amplifier-indicator. A load (weight) is applied to the weight tray (by means of an overhead pulley), and the depth of indentation is recorded as a function of time. After a specified period of time, the load is removed and the recovery is recorded.

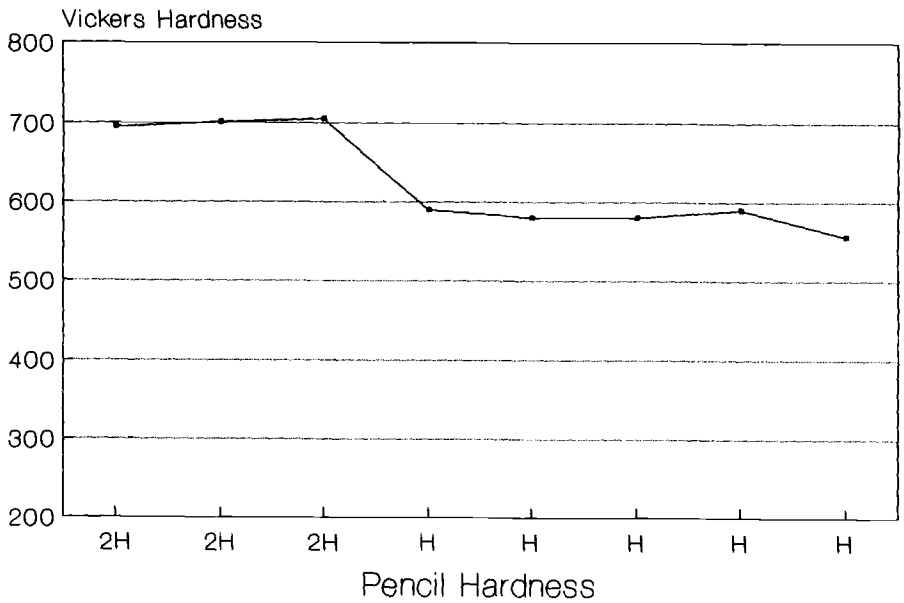

FIG. 18–Comparison of Vickers hardness versus pencil hardness.

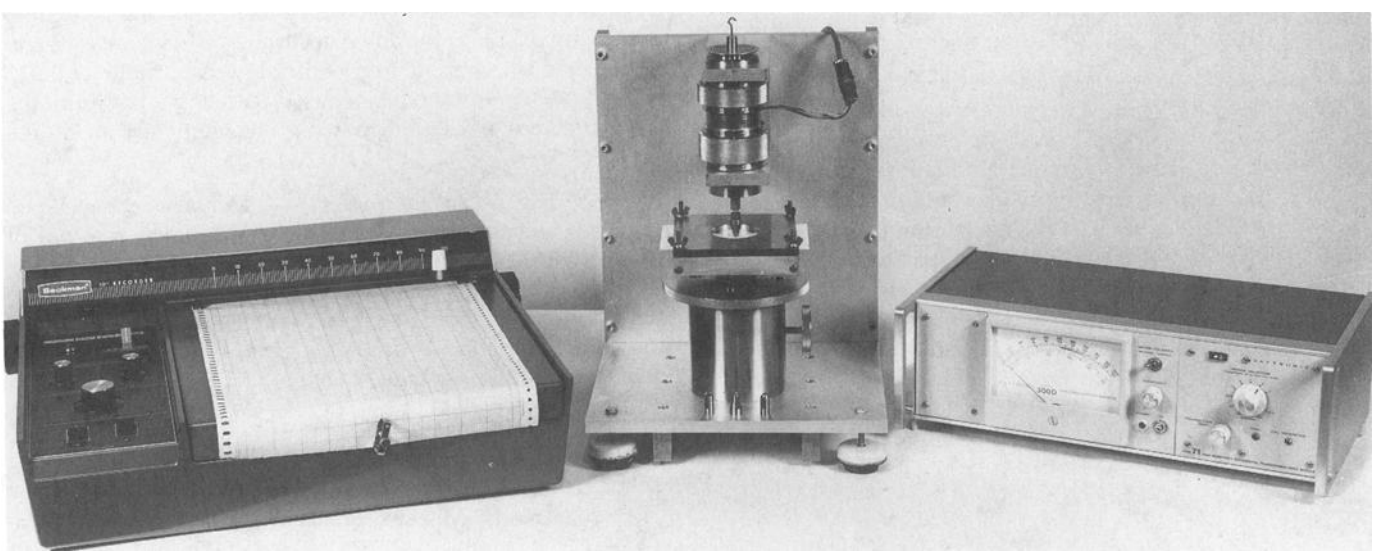

FIG. 19–Bell Telephone Laboratories Indenting Rheometer.

Brinell Indentation Hardness Tester—In 1900, J. A. Brinell published the results of his tests that involved pressing steel balls into materials [*41*]. The Brinell test is based on the following formula

$$H = \frac{P}{\frac{\pi D}{2}(D - \sqrt{D^2 - d^2}} \quad (5)$$

The relationship between the hardness H and the diameter of the depression d has been worked out on a form for a given size steel ball whose diameter is D.

Buchholz Indention Hardness Tester—This device, shown in Fig. 20, is made by the Erichsen Company [*42*] and has been standardized in Germany [*33*]. It is a simple, portable instrument and, like the Knoop, measures the length of the recovered indent impression after the load has been removed. In fact, the resultant impression, though much larger, is quite similar in appearance to the Knoop impression.

A diagram of the Buchholz Indention Hardness Tester in use is shown in Fig. 21. Basically a weighted (500-g) wheel, with an included angle of 60° from center to each edge (total angle of 120°), is placed on a coated test panel. The test panel is marked "5" in the diagram, and the coating is marked "4." The wheel is removed, and the length of the impression made by the indenter, marked "3" in the diagram, that remains is measured by means of a small, ×20 microscope, marked "2" in the diagram, and an attached light source, marked "1" in the diagram. To facilitate measurement, the impression is illuminated from the side, thereby creating a shadow in that side of the impression. The impression may be measured to within 0.05 mm (compared to 0.001 mm for the Knoop).

CDIC Hardness Penetrometer—Still another variation applied to artists' colors is the CDIC (the old Cincinnati-Dayton-Indianapolis-Columbus Paint and Varnish Production Club) Hardness Penetrometer [*43*]. A diagram of it is shown in Fig. 22. By this device, a ½-in. chisel is caused to penetrate the film that has been applied to metal. Chisel and metal are wired in series with an electric bulb, which lights up when the chisel contacts the panel. The instrument was never commercialized.

Fischerscope® Microhardness Tester[2]—The Fischerscope® H100V, shown in Fig. 23, is a dynamic microhardness tester which can be used on a variety of materials, including coatings, to measure hardness under load. It works with very small test loads up to 256 mN. Determination of hardness based on the plastic and elastic deformation of a material is the direct result of measurements under load. Hardness measurement is expressed in N/mm^2, corresponding to the quotient of load P over area of impression A (whereby A can be derived directly from the depth of indentation). This definition of hardness is physically meaningful by providing a measurement of hardness to an uncertainty of ±1%. This requires exact measurement of load and indentation depth, which is possible with a Fischerscope® H100V Microhardness Tester.

[2]Available from Fischer Technology, Inc., 750 Marshall Phelps Rd., Windsor, CT 06095.

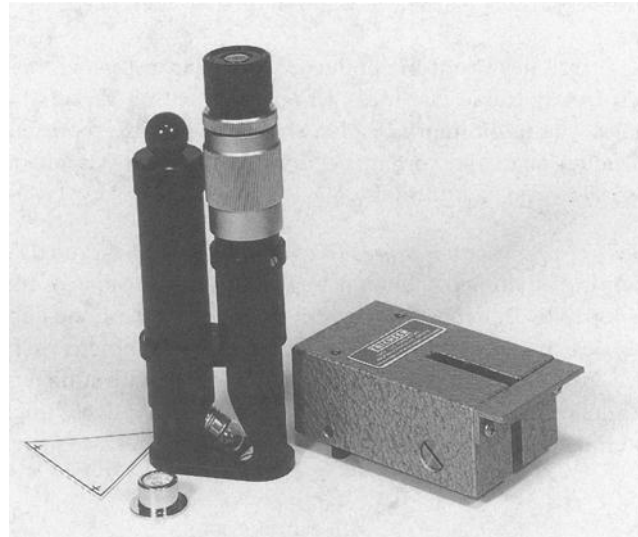

FIG. 20–Buchholz Indention Hardness Tester. (Courtesy of Erichsen GMBH & Co.)

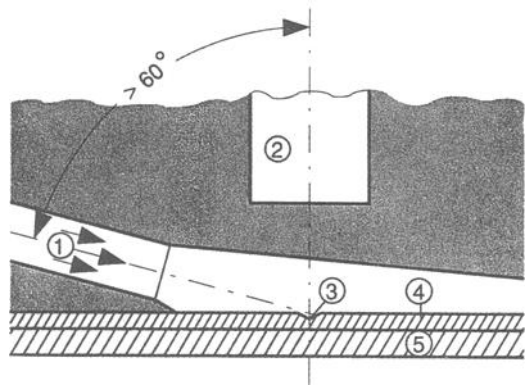

FIG. 21–Buchholz Indention Hardness Tester in use. (Courtesy of Erichsen GMBH & Co.)

Using a Fischerscope® H100V Microhardness Tester, W. W. Weiler developed a dynamic, nondestructive test method to measure the microhardness of surface layers, coatings, and homogeneous materials in the ultra-low load range of 0.025 to 1 N [*44*]. The method was based on using a conventional Vickers indenter coupled to a displacement measuring device.

General Electric Indention Tester[3]—This device, developed by C. Dantsizen, consists of a dial micrometer, the foot of which terminates in a metal sphere 0.20 in. (5 mm) in diameter, and with means for applying a load. The depth of indentation is read on the dial. The General Electric Indention Tester was not widely used within the General Electric Co. nor did it gain industry acceptance.

ICI Pneumatic Microindenter—This commercially available device,[4] shown in Fig. 24, was developed by Monk and

[3]Christian Dantsizen, personal communication to G. C. Sward, 1938.

[4]Available from Research Equipment (London), Ltd., 64 Wellington Road, Hampton Hill, Middlesex, England.

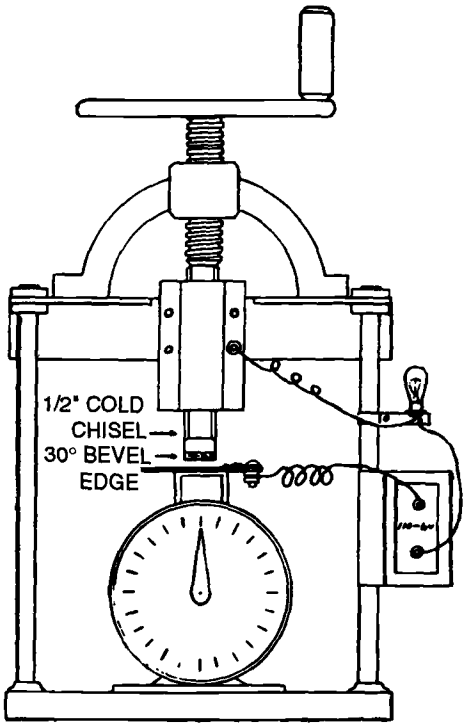

FIG. 22–CDIC Hardness Penetrometer.

Wright [*45*]. As the name implies, it is a pneumatic type (air pressure) instrument that measures and records the depth of indentation or penetration of a ball-ended needle under the application of a constant load and the recovery subsequent to removal of the load. The needles have steel or sapphire ends and vary from 0.0025 to 0.063 in. (1.6 mm) in radius. A preload of 0.1 g must be applied. A 5-in. (12.7-cm), pneumatically operated, strip-chart recorder provides curves of the indentation and recovery thereof. An indenter movement of 6 μm causes a full-scale deflection on the recorder. A calibration knob is divided into 0.5-μm divisions, thereby giving an accuracy of about 0.2 μm (0.008 mil).

However, the chart can be read to within 0.1 μm (0.004 mil). The specimen stage or table is a Frigister unit which can raise or lower the specimen temperature. Disadvantages are that it is not a sturdy instrument and must be handled with some care. The panel or specimen must be small enough to fit on the rather small Frigister stage. Also, the use of relatively sharp indenters (referred to by the authors as needles) means that, in many cases, the organic coating will be cut or penetrated, yielding spurious results.

The load limit appears to be less than 100 g, and the design does not appear to be conducive to the use of commercially made Knoop or Vickers pyramid indenters. Finally, results obtained using the Frigister to heat or cool the specimen can be misleading. If the indenter is at room temperature, then the specimen temperature where the indenter contacts will not be the same as the temperature of the Frigister. However, the ICI pneumatic microindentation apparatus was still the first commercially available instrument that appears to have the sensitivity necessary to be seriously considered as an indenting rheometer suitable for use with organic coatings. Monk and Wright gave some results obtained from the use of the apparatus and went further than Gardner et al. [*46*] in the interpretation and meaning of the curves. Included in the data were curves showing how an alkyd finish changed properties as a function of temperature and accelerated weathering.

Knoop Indenter—At the National Bureau of Standards (now known as the National Institute of Standards and Technology), Frederick Knoop and his associates [*47*] developed a diamond-based pyramid indentation tool as an improvement over the Vickers indenter. This indenter gave well-defined indentations and reproducibility of results when testing glass and crystals of the Mohs scale, and dental plastics and enamels.

The Knoop indenter, illustrated in Fig. 25, is a pyramidal diamond with included longitudinal angles of 172° 30′ and an included traverse angle of 130° 0′. It produces a diamond-shaped (rhomb) indentation having long and short diagonals of an approximate ratio of 7 to 1. The depth of indentation is about 1/30th of its length. In essence, the Knoop indenter is a shallow double wedge. The Knoop indenter is subsequently mounted in a machine which applies a load, without impact, at a constant rate and has a microscope equipped with a filar eyepiece for measuring the size of the indentation within ± 1%. Although the Knoop indentation hardness method was developed originally for measuring the hardness of metals, shortly thereafter Lysaght [*48*] suggested its use for organic coatings. Gusman [*49*] reported on its use for organic coatings. The instrument was specified in ASTM D 1474, adopted in 1957.

In its use for organic coatings, a load of 25 g is applied for 18 s, after which time the indenter is removed from the coating, and the length of the long diagonal of the impression remaining in the coating is measured as quickly as possible. This dimension is then used to obtain the Knoop Hardness Number (KHN), which is the ratio of the load, in kg/mm^2, to the projected planar area.

$$KHN = \frac{L}{A_p} = \frac{L}{lC_p} \tag{6}$$

where

L = load in kilograms applied to the indenter,
A_p = projected area of indention in mm^2,
l = measured length of the long diagonal of the indentation in mm, and
C_P = indentor constant relating l to A_p, usually 7.028×10^{-10}.

Most writers refer to l and A_p as the unrecovered length and area, but as we shall see later, this is not true. Elastic recovery of the indentation impression takes place the instant the indentor is removed, and substantial viscoelastic recovery takes place before a measurement can be made.

The real difference between the Pfund and Knoop methods is that with the Pfund, the hardness measurement is made when the indenter is under load, while with the Knoop the measurement is made of the indentation impression remaining after both the load and indenter have been removed. This remaining Knoop impression is smaller than the original made while under the loaded indentor because all of the elastic and substantially all of the viscoelastic (creep) recovery occur in the indentation impression once the load is

removed. This will be explained and actually shown in the subsection on theory.

Therefore, the operation of the Pfund and Knoop methods rests on two entirely different principles. Each measurement represents a completely and substantially different point on a viscoelastic creep-creep recovery curve for any given material or organic coating (see Fig. 26). Yet, the amazing part is that, quite coincidentally, the numerical results can be quite similar. This similarity in numerical results (PHN ≈ KHN) with organic coatings probably could never have been achieved deliberately. How fortunate for the paint industry that the equivalence exists.

Of the two test methods, the Modified Pfund and the Tukon gage with the Knoop indenter, the former is a dynamic hard-

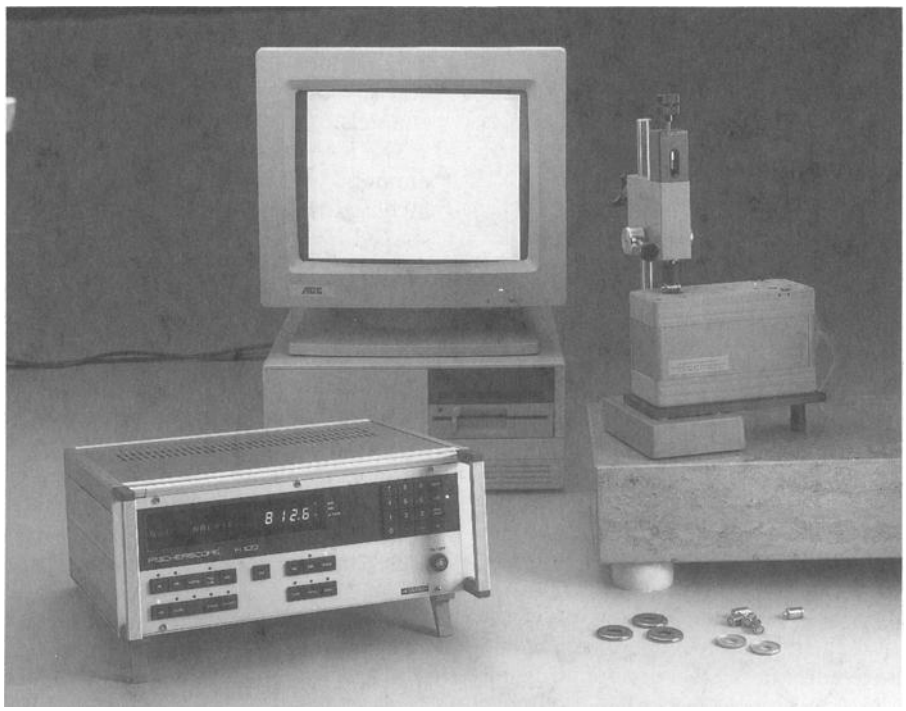

FIG. 23–Fischerscope® H100V Microhardness Tester. (Courtesy Fischer Technology, Inc.)

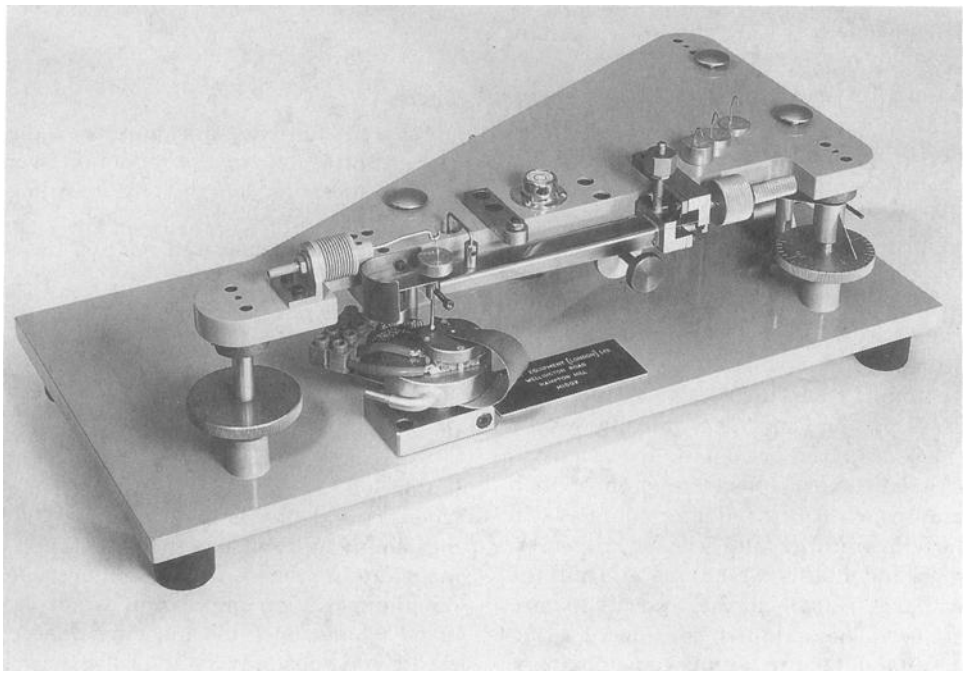

FIG. 24–ICI Pneumatic Microindenter. (Courtesy Research Equipment (London), Ltd.)

FIG. 25–Diagram of Knoop Diamond Indenter.

ness test and the latter is a static hardness test. Those in the automotive industry know how difficult it can be to obtain repeatable Knoop hardness numbers on metallic finishes. Secondly, with some types of finishes, the ends of the long diagonal of the Knoop impression recover, yielding rounded ends. In others, the organic finish sometimes recovers in such a manner as to partially close the indent near the ends of the long diagonal. However, the main reason for this preference is that the Pfund measures the indent under load. That is when the coating is resisting the indentation.

Pfund Hardness Tester—After numerous, unsuccessful attempts to grade the hardness of varnishes by means of the scratch test in which graded pencils, crystals, etc. were used, A. H. Pfund, an associate professor of physics from Johns Hopkins University, Baltimore, MD, modified the Brinell Indention Test [*50*]. In this method the measurements are made on the organic coating while the loaded indentor is in contact with the coating. At first a 1/16-in.-diameter steel ball was forced under load into the varnish, and the diameter of the resultant circular impression was measured under the microscope. This was soon changed to a quartz cylinder terminating in a hemisphere 1/4-in. (6 mm) in diameter. The results are expressed as the load on the indentor, in grams, necessary to achieve a specified diameter of indent. The device, shown in Fig. 27, consists of a counterbalanced brass beam containing the Indenter C. Illuminating light is reflected into the indenter by the clear Glass G and reflected back up to the Microscope 0, where the planar diameter of indent is measured by means of a filar eyepiece (shown in the upper right hand corner of Fig. 27). The results are expressed as the load on the indentor, in grams, necessary to achieve a specified diameter of indent. Table 3 shows typical results at an indent of 3 divisions (each division is approximately 0.1 mm). Additional data can be found in the work by Pfund, and Schuh and Theuerer [*51,52*].

In making a hardness determination, instead of attempting to find the exact load necessary to produce the specified diameter of indent, it was preferable to apply loads producing diameters both greater and less than the value sought and then interpolate to the specified diameter. However, this method is not precise because the relationship between load and diameter is not linear. Although this method of always achieving the same indent results in geometrically similar indents in all cases, this theoretical consideration of geometrically similar indents is significant only when the material being measured is thick enough for the hardness measurement to be uninfluenced by the thickness of the material. Such is not the case here. The theoretical consideration of geometrically similar indents will be discussed in the subsection on theory.

As this method was rather tedious and time consuming, the instrument and method were modified in the early 1950s by the Bell Telephone Laboratories. The modified Pfund and test method were incorporated into ASTM D 1474 [*53*]. The Modified Pfund device is shown in Fig. 28. The instrument devel-

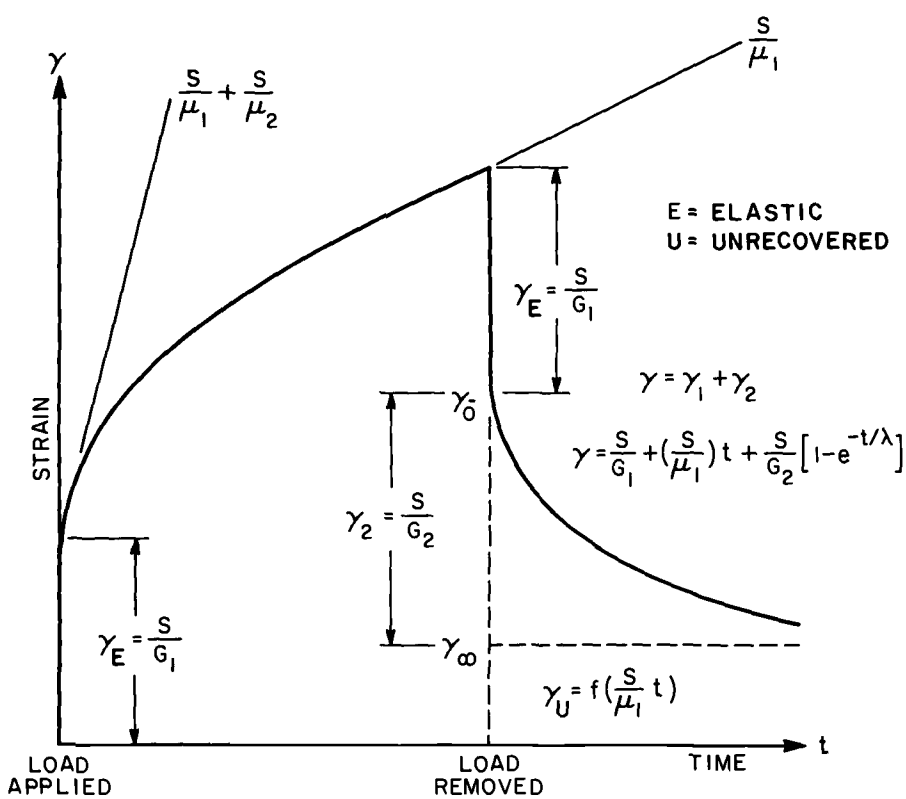

FIG. 26–Creep and creep recovery curves of viscoelastic material.

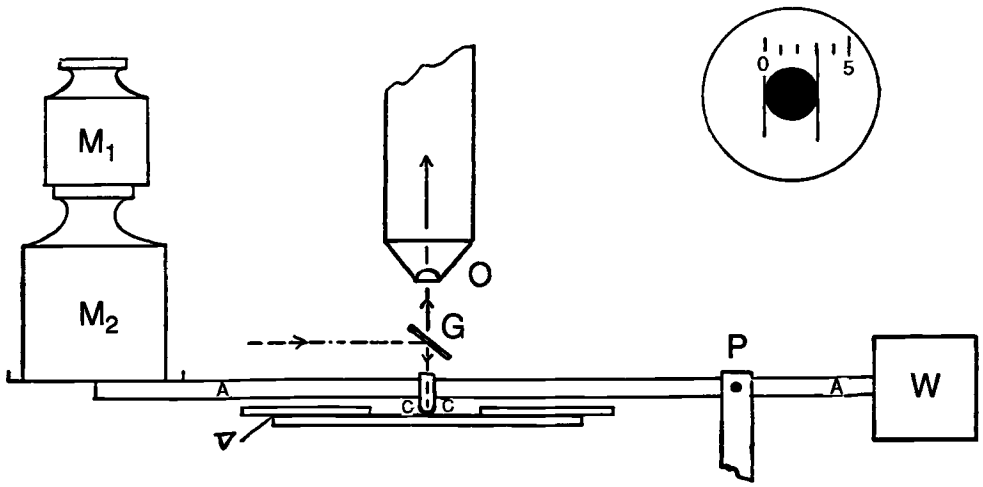

FIG. 27–Diagram of Pfund Hardness Indenter.

oped at the Bell Telephone Laboratories and initially adopted by the ASTM as Method D 1474 is shown in Fig. 29.

The indenter is a transparent, colorless synthetic quartz or sapphire hemisphere whose spherical radius is 0.125-in. (¼-in.) (6 mm) diameter with a maximum spherical eccentricity of 0.002 in. (0.05 mm). The indenter is mounted in a holder weighing 1000 g so that the indenter is always under a load of 1000 g when making measurements. Hence, we see that in this method the load is kept constant and the resultant diameter of indent is recorded. This is exactly opposite to the original Pfund method.

In operation, the test panel is brought into contact with the loaded indenter, and after 60 s (while still under load) the diameter of the circular impression is measured by means of a filar micrometer mounted in the eyepiece of the microscope. Each filar division represents 0.1 mm, and the diameter of the impression is converted into a Pfund hardness number (PHN), expressed in kg/mm^2 units, as follows

$$PHN = \frac{L}{A} = \frac{L}{\frac{\pi d^2}{4}} = \frac{1.27}{d^2} \tag{7}$$

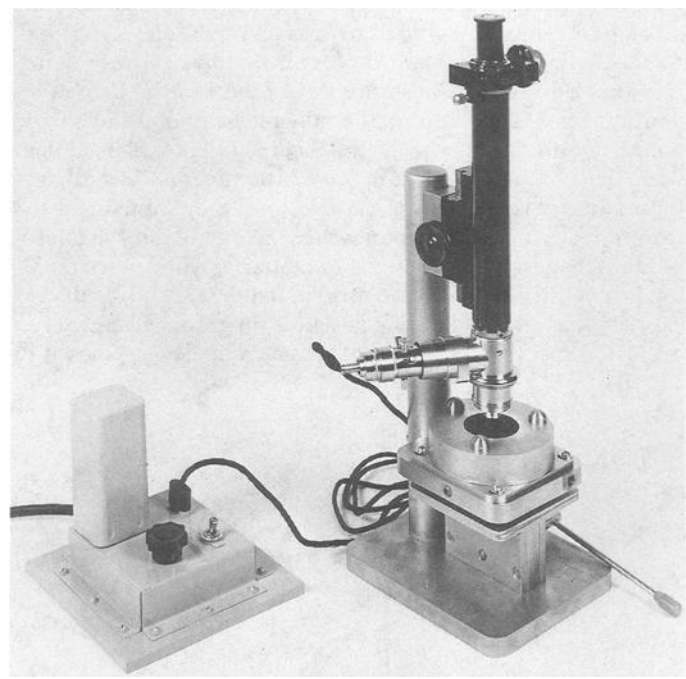

FIG. 28–BTL designed modified Pfund Hardness Gage.

TABLE 3—Pfund hardness.

Coating[a]	Thickness, mil	Hardness at Three Divisions
A	0.7	730
	1.3	380
	3.0	47
B	0.6	435
	1.1	130
	3.5	<5
C	0.5	188
	1.0	35
	1.8	<5
H	0.6	875
	1.1	720
	3.1	370

[a]A = 10-gal ester-gum varnish, B = ester-gum varnish at 25 gal, C = ester-gum varnish at 40 gal, H = lacquer enamel.

where

L = load in kilograms (1 kg) applied to the indenter,
A = planar or projected area of indention in square millimeters, and
d = diameter of the indentation in millimeters.

Therefore, the PHN is the load, in kilograms, divided by the planar or projected area of indentation.

The planar or projected area of indent deserves some explanation and was covered in detail in the introduction. Figure 30 illustrates what is meant by this for the case of a spherical indentor where the hardness measurement is made while the hemisphere is under load and in contact with the coating. Initially the hardness or PHN was reported as 10d. The reason for changing it to the load divided by the planar area of indentation was to make the reported PHN results have the same units of measurement as the Knoop hardness number

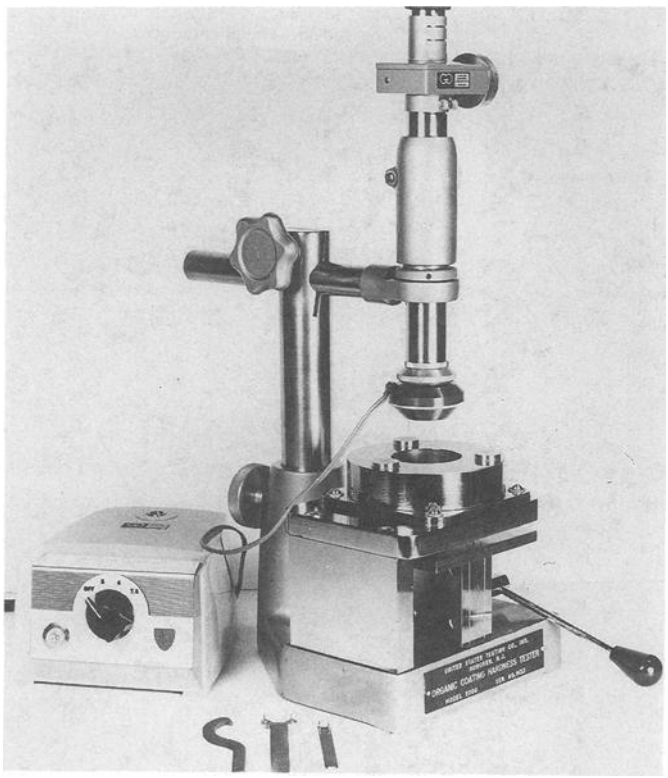

FIG. 29–Commercial modified Pfund Hardness Gage.

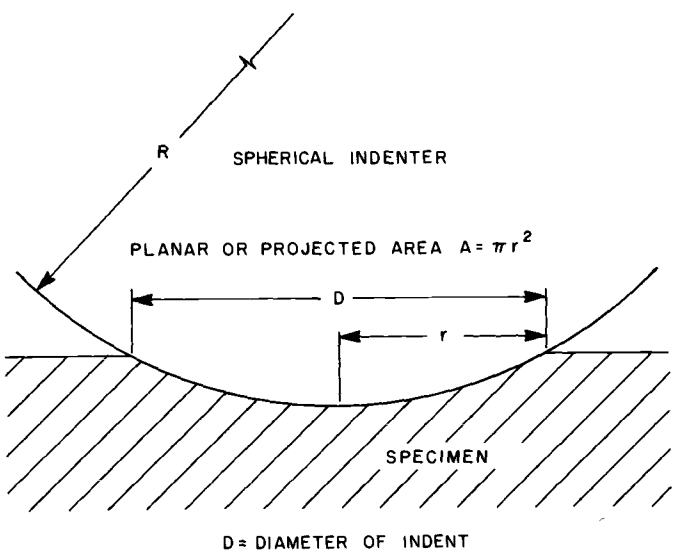

FIG. 30–Planar area of contact of the Pfund Indenter.

(KHN) also in ASTM Method D 1474. Surprisingly, the PHN and KHN values come very close numerically.

Rockwell Hardness Tester—Indentation hardness tests have been used as a means of checking the uniformity of the mechanical properties of metals since the 19th Century. The Rockwell Hardness Tester began as a hard steel conical indenter having a hemispherical tip of 0.50 mm in diameter. It was first used by Hugueny (1865) during his patent studies of hardness [*54*]. The machine was improved when Wilson in 1926 produced his polished spheroconical diamond indenter where the cone had an included angle of 120° and the tangential spherical tip of 0.40 mm in diameter.

Wilson®/Tukon® Hardness Tester[5]—Vincent E. Lysaght of Wilson Mechanical Instrument Co. took the work of the late Frederick Knoop and applied the technique to the testing of nonmetallic materials ranging from plastics to diamonds [*48*] using their Tukon Hardness Tester.

The Wilson®/Tukon® Microhardness Tester offers a variety of possibilities as a tool in research and development, materials testing, and quality control program. Some coating manufacturers use the Sward Hardness Tester to get approximate hardness values but rely on this tester to qualify a coating. It can be fitted with either a Vickers or a Knoop indenter. A comparison of these two indenters is shown in Fig. 31. A Knoop indenter is typically used to measure the hardness of coatings, whereas the Vickers indenter is used for hardness testing of harder materials such as metals.

This instrument, with the precision of x-y stage, makes it possible to locate indentions with great accuracy. The instrument has undergone many refinements such as having a computer controlled X-Y Auto Traversing Stage System and a software program for running statistical process analyses. One of their latest instruments is shown in Fig. 32.

Wallace Microhardness Tester H-7[6]—The Wallace Microindention Tester [*55*], like the Wilson®/Tukon® Hardness Tester, can also employ a Vickers diamond pyramid indentor and uses a capacitive form of measurement to determine the depth of indention under load. Figure 33 shows the Wallace tester. This instrument measures the depth of penetration of an indentor into a material under a known load, the depth of penetration being a function of that indicated on a dial gage.

Basically, the instrument consists of an indentor, supported by leaf springs, attached to a parallel plate capacitor which forms one half of a capacitance balance circuit. When no load is applied, the indentor "floats" in a "null" position, electronically balanced by the second half of the capacitance balance circuit. This "null point" (i.e., the point of electrical balance) is indicated by a zero reading on the center zero meter located in the base of the instrument.

The test panel is supported on a table that is raised or lowered by means of an accurately made wedge. The dial micrometer gage follows and indicates the lateral movement of the wedge which is, in turn, converted to vertical movement of the table. Primary loads of usually less than 1 g and secondary loads between 1 and 300 g are placed on the weight platform, which, in turn, is attached to the indenter.

In operation, the instrument is first set to a zero position, and a test panel is placed on the specimen table or stage. The panel is raised to the indenter. The primary load is applied to the indentor, and the system is once again zeroed. The secondary load is applied for the predetermined time during which the panel is raised to maintain the indenter in its zeroed position. At the end of the predetermined time, the reading on the gage is taken and the corresponding depth of indentation is obtained by dividing the gage reading by the wedge ratio (20 to 1 or 40 to 1). The Wallace Microhardness Tester was

[5]Available from Wilson Instruments, 6 Emma Street, Bingham, NY 13905.

[6]Available from H. W. Wallace & Co., Ltd., St. James Road, Croydon, England and Testing Machines, Inc., 400 Bayview Avenue, Amityville, N.Y. 11701.

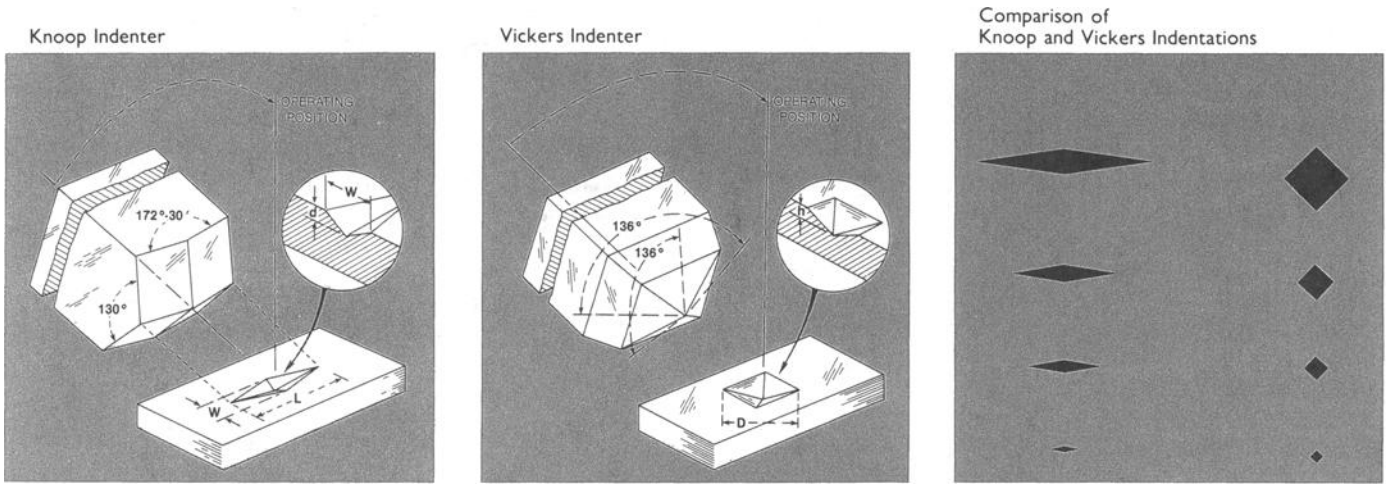

FIG. 31–Comparison between a Knoop and Vickers Indenter. (Courtesy Wilson Instruments, Inc.)

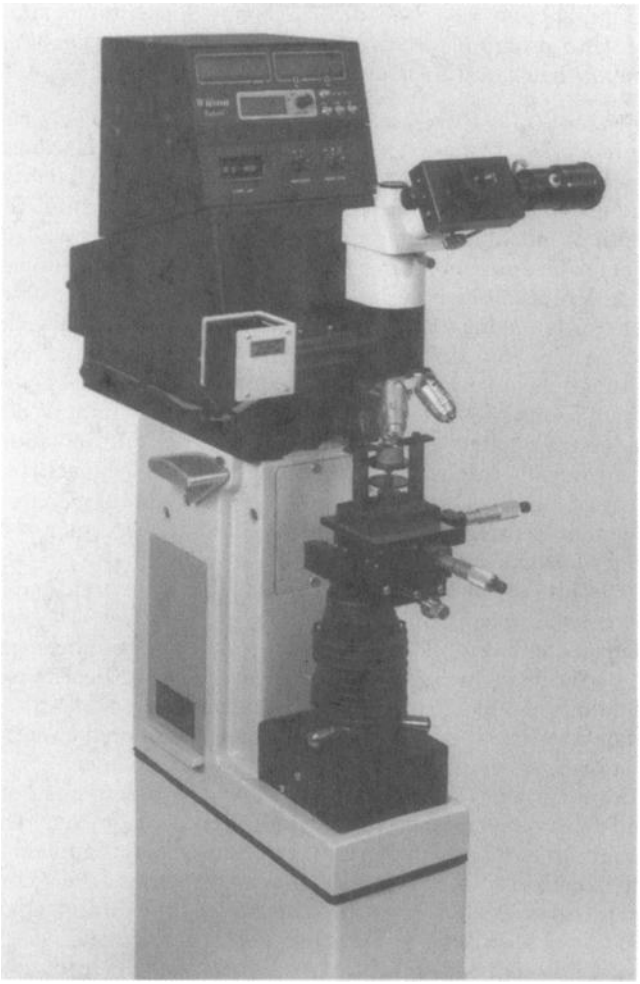

FIG. 32–Wilson®/Tukon® Hardness Tester. (Courtesy Wilson Instruments, Inc.)

FIG. 33–Wallace Microhardness Tester H-7. (Courtesy of H. W. Wallace & Co., Ltd.)

used in a cooperative investigation by the Manchester Section of the Oil and Colour Chemists' Association [*56*] and is commercially available. According to Fink-Jensen [*57*], it is possible to obtain an accuracy of 0.3 to 0.5 μm or about 0.01 to 0.02 mil.

Indentation Hardness Miscellaneous

Imprint Resistance—Organic coatings for chairs, desks, and other furniture often appear hard, but when subjected to continuous pressure they may creep, yield, or flow enough to be permanently and seriously damaged. Print resistance is a measure of this phenomenon. The print resistance of an organic coating should be related to its glass transition temperature, *Tg*. Andrew Mercurio discussed this viscoelastic

behavior of polymers at length in his article [37]. Expressed mathematically

$$B = \frac{P}{\frac{\Delta V}{V}} \tag{8}$$

$$E = \frac{F/A}{\Delta l/l} \tag{9}$$

$$G = \frac{F/A}{\theta} \tag{10}$$

where B is the bulk modulus expressed in terms of the applied pressure, P, the initial volume, V, and the decrease in volume, ΔV. In tension, we obtain Young's modulus, E, given in terms of the applied force, F, per unit of original cross-sectional area, A, the original length, l, and the change in length, Δl. The shear modulus, G, is also expressed in terms of the applied force per unit original cross-sectional area and the angle of deformation, θ. In each case the numerator is termed the stress and the denominator is defined as the strain. Only two of these moduli represent independent properties of the isotropic material in question since the moduli are related through the Poisson ratio, ν.

$$E = 2(1 + \nu)G \tag{11}$$

$$B = \frac{E}{3(1 - 2\nu)} \tag{12}$$

This simple, basic method was adopted by the Federal Government (Federal Test Method Standard No. 141, Method 6211, Print Test). However, in 1980, the federal government canceled this test method in favor of an ASTM test method (D 2091: Test Method for Print Resistance of Lacquers). Another ASTM test method is Test Method D 1640: Test Methods for Drying, Curing, or Film Formation of Organic Coatings at Room Temperature. Print resistance may be evaluated by the load required to make an impression within a given time, the time required under a given load, or by comparing the imprint under identical loads and duration of test. The temperature may also be varied. This test is sometimes used as a drying time test.

Twisting Cork Tester—This device [58], shown in Fig. 34, was an attempt to simulate a thumb being pressed on a film and then twisted. It consists of a cork at the lower end of a vertical rod upon which may be placed varying weights. By means of an arm in the rod, the cork can be turned or twisted through any desired angle.

The average reader may consider that perhaps this device belongs in the section on drying time. However, it was developed for measuring the hardness of oils and oil mixtures, which can be soft enough to defy the use of more conventional methods.

Pendulum-Rocker (Damping) Hardness

A few pendulum hardness tests are in use by the coating industry. The Sward Rocker Hardness Test is widely used in the United States; The König Pendulum Test is commonly used in Germany and Europe; and the Persoz Pendulum Test

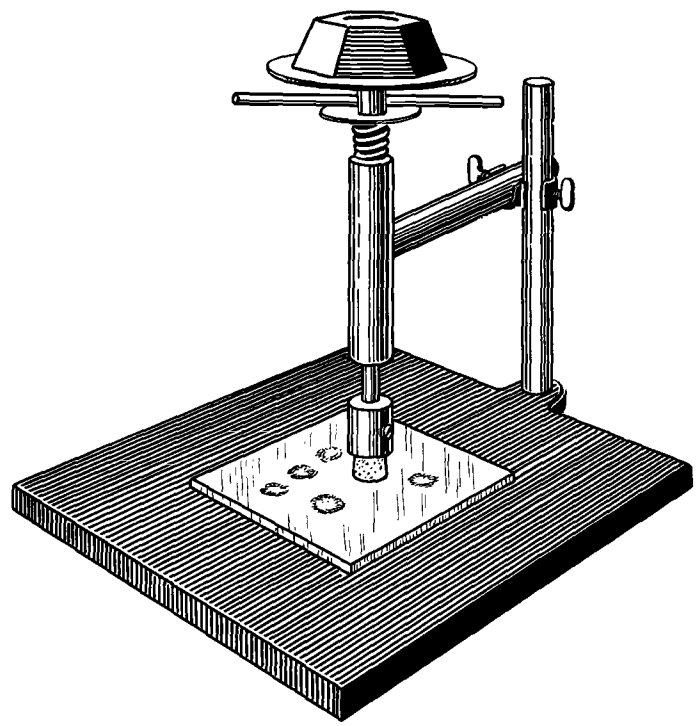

FIG. 34–Twisting cork hardness tester.

is employed for coating hardness testing in France and Europe. The specific apparatus employed in these methods is different, but, in principle, the tests are the same. These tests are described below.

The pendulum hardness tests are closely related to the Sward Rocker Hardness Test. The hardness pendulum rests on the test surface and pivots on two hardened steel balls. The time required for the pendulum to decay from some initial amplitude to some final amplitude is a measure of the hardness of the coating film.

The theory of the pendulum or rocker hardness testing was derived by Persoz [59]. Pierce et al. [60] made a detailed experimental investigation of the Sward Rocker Hardness Test. The observed mechanics of the Sward Rocker were found to be in complete agreement with the Persoz analysis. The Sward hardness of a coating was found to be influenced by temperature, humidity, film thickness, substrate hardness, and air pressure. Coefficient of rolling friction values were recovered from the values of Sward hardness and the physical parameters of the rocker. The coefficients of rolling friction are related to the shear modulus and loss tangent of the coating. The analysis shows that if the physical parameters of different rockers or hardness pendulums are known, it is possible to relate the hardness values obtained on different instruments.

Pendulum or damping is the least understood hardness test method. A pendulum supported on the specimen by a ball or cylinder was applied to hardness testing by Le Rolland [61] and can be used to measure strain hardenability. Similarly, the Herbert Pendulum Tester [62] employed the strain-hardenability principle to measure hardness. The Herbert Pendulum Tester consists of a 4-kg arched casting which is supported on the horizontal plane surface of the specimen by a 1-mm-diameter ball. The ball can be either hard steel or

diamond. In a pendulum hardness test, an inverted compound pendulum is supported on a hard steel ball which rests on the metal under examination. The hardness is measured by the damping produced as the pendulum swings from side to side. When applied to polished plate glass, the pendulum oscillates so that ten single swings requires 100 s. If the device is then placed on a specimen of lead, the time hardness (for ten swings) is only 2 to 4 s, and other metals give intermediate values. This device does not apply to measuring coating hardness, but those described below use this pendulum principle.

König Pendulum—The König pendulum hardness tester [*63*] is currently manufactured in England by Sheen, Ltd. and in Germany by Erichsen GMBH & Co. The one shown in Fig. 35 is manufactured by Sheen, Ltd. It uses the damping properties of organic surfaces (e.g., paints, coatings, plastic materials, films of all kinds, and paper) to determine the hardness. The measurements are so sensitive that the drying process of layers of paint can be followed from the start of the drying to complete hardening. It has been standardized in the United States and Germany. It is in accordance with ASTM D 4366: Test Method for Hardness of Organic Coatings by Pendulum Damping Tests, DIN 53 157, ISO 1522, Association Suisse de Normalisation (SNV) 37 112, and National Federation of Textiles (NFT) 30 016 for pendulum hardness test instruments.

In its operation, the oscillations of a standard pendulum supported on the test surface by balls are dampened more strongly on softer surfaces. The degree of dampening is measured by the time in seconds taken for the amplitude of the pendulum to diminish from the initial to the final value. It is described in the ISO Recommendation 1522 as follows:

> The pendulum rests on two stainless steel balls, 5 ± 0.005 mm diameter, of hardness HRC 63 ± 3, 30 ± 0.2 mm apart, and is counterpoised (to adjust the natural frequency of oscillation) by means of a weight sliding on a vertical rod attached to a cross bar. The period of oscillation should be 1.4 ± 0.2 s on a polished plate glass panel; the time for damping from a 6° displacement to a 3° displacement, on the same substrate, should be 250 ± 10 s. The total weight of the pendulum should be 200 ± 0.2 g.

Persoz Pendulum—Persoz designed the pendulum hardness tester [*59*] shown in Fig. 35. It is manufactured in Germany by Erichsen GMBH & Co. It was a result of Persoz's mathematical analysis and experimental studies. It is written up in the ISO Recommendation 1522 as follows:

> The pendulum rests on two stainless steel balls, 8 ± 0.005 mm diameter, of hardness HRC 59 ± 1, 50 ± 1 mm apart. A counterpoise is not provided. The period of oscillation should be 1 ± 0.001 s on a polished plate glass panel and the time for damping from a 12° displacement to a 4° displacement on the same substrate should be at least 420 s. The total weight of the pendulum should be 500 ± 0.1 g, and its center of gravity at rest should be 60 ± 0.1 mm below the plane of the fulcrum, the pointer tip being 400 ± 0.2 mm below the plane of the fulcrum.

The Persoz pendulum is prone to skidding on surfaces having a low coefficient of friction. However, compared to the König pendulum, the Persoz pendulum is particularly useful with relatively soft organic coatings. This is a result of longer damping time of the Persoz pendulum (about two times that of the König), which makes it more sensitive to small differences between soft organic finishes where the damping times are relatively short. The Persoz pendulum has been standardized: United States, ASTM D 4366; France, NTF 30 016.

A comparison of similarities and differences between the König and the Persoz pendulum hardness instruments is shown in Table 4. BYK-Gardner, Inc. distributed a graph which compares König hardness values with Persoz hardness values. This graph is shown in Fig. 36. The source of the data is reputed to be from Volkswagen Co.

Rolling Ball Hardness Tester—Dr. Howard Moore devised a rolling ball tester at the Navy Yard Laboratories in Philadelphia. A description of it appears in the 11th edition of *Gardner/Sward Physical and Chemical Examination of Paints, Varnishes, Lacquers, and Colors,* 1950. The device was used to evaluate the drying times of coatings and measured the time required for a small steel ball to roll a fixed distance over the coating. Using this principle, a new instrument for testing hardness properties using the rolling ball concept. It is shown in Fig. 37 and is marketed by the Paul N. Gardner Co. under the name Gardco Rolling Ball Hardness Tester. The instrument utilizes a 1.5-in. (38 mm) diameter steel ball confined in a raceway about 6 in. (15 cm) long, all mounted on a platform which may be accurately tilted by an electrical solenoid. Mounted at each end of the raceway is an electrical sensor for detecting the presence of the ball. The raceway assembly tilts to an equal and opposite incline whenever the ball is detected at the low end of the raceway. An electrically actuated timer is connected to register the number of seconds required for the

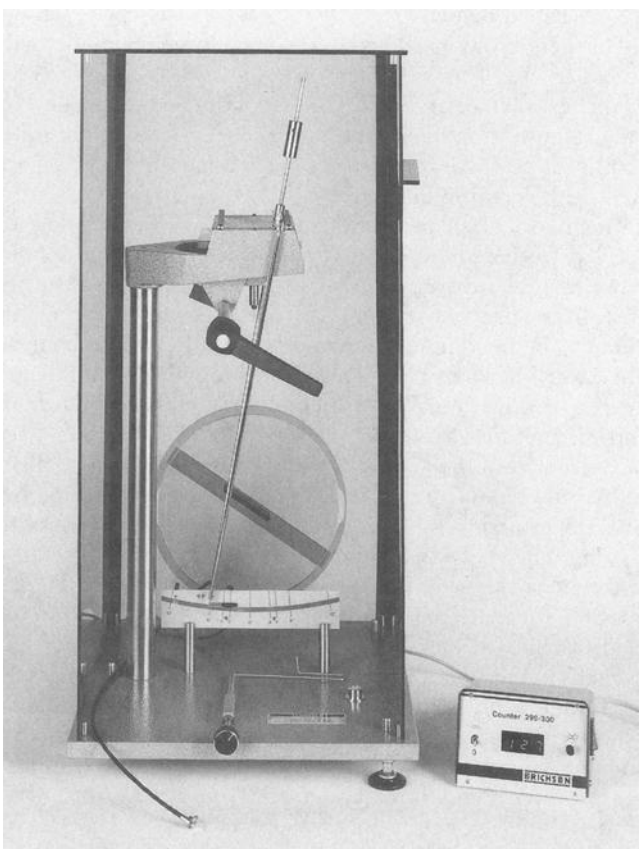

FIG. 35–König/Persoz Pendulum Hardness Tester.

TABLE 4—Comparison of König and Persoz hardness testers.

	König	Persoz
Weight	200 ± 0.2 g	500 ± 0.1 g
Ball diameter	5 mm/0.2 in.	8 mm/0.3 in.
Deflection:		
Start	6°	12°
End	3°	4°
Period of oscillation (1 oscillation)	1.4 s	1 s
Damping time on glass	250 ± 10 s	420 ± 10 s

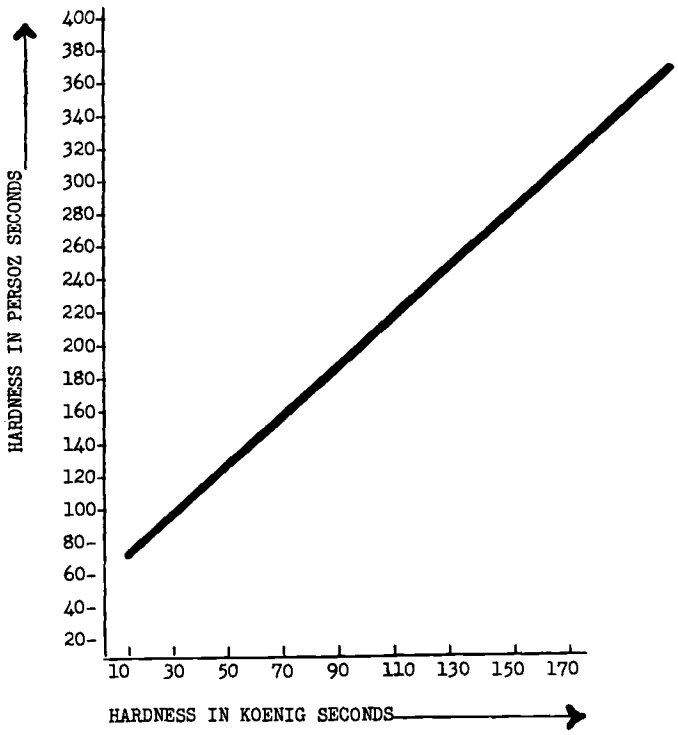

FIG. 36–Comparison of König hardness values versus Persoz hardness values.

ball to complete a set number of complete cycles of the ball in the raceway. Specimens up to 12 in.^{2} (77.4 cm^2) and up to ½ in. (12.7 mm) thick are accommodated, and the new tester should find application in evaluating coated sheet metal, woven products, coated wood, floor coverings, paper, and leather.

Sward Rocker Hardness Tester—George Gilbert Sward was awarded a patent [*64*] for his coating hardness tester that was developed when he was associated with the National Paint, Varnish, and Lacquer Association [*65*]. This is shown in Fig. 38. It is perhaps the best known and most widely studied instrument for measuring the hardness of organic coatings. ASTM Committee D-20 on Plastics wrote a standard using the Sward hardness tester, D 2134. Committee D-20 turned over the responsibility of D 2134 to Committee D-1 in 1991. They are in the process of rewriting D 2134 and will be developing data for the Precision and Bias statement since many coatings companies use the instrument on a daily basis.

As to its operation and use, the following is from the 12th edition of this manual [*66*]:

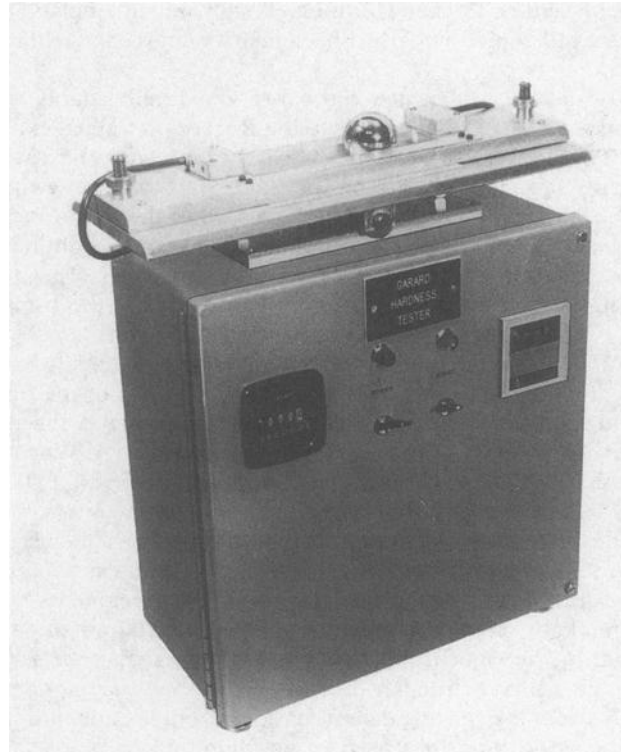

FIG. 37–Rolling Ball Hardness Tester. (Courtesy of The Paul N. Gardner Company, Inc.)

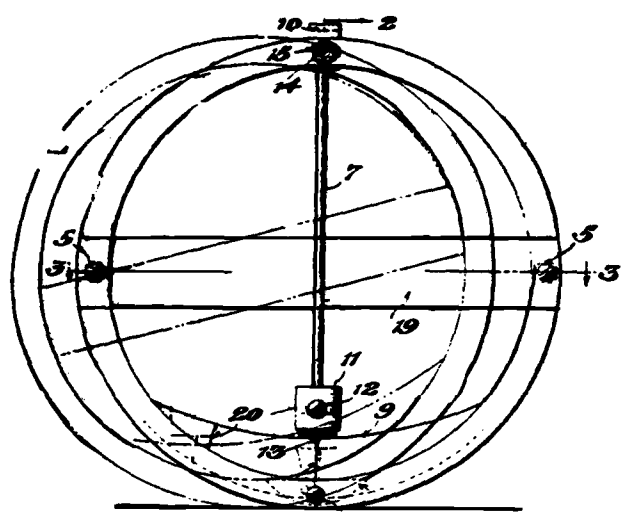

FIG. 38–George Sward's Original Rocker Hardness Tester. (From the patent.)

The Rocker operates on the same principle as does the Swinging Beam and other pendulums. However, it is self-contained and requires no separate scale. Some models also have their own circular level. It consists of two flat, 4-in. chromium-plated, bronze rings, spaced 1 in. (25.4 mm) apart. Amplitudes of oscillations are indicated by two tube-style levels in the lower half. The level at the left is for marking the start of a test; the one on the right for marking the end.

At the present time, Sward-type rocker hardness instruments are manufactured in Germany by Erichsen as the

Sward-Zeidler Rocker Hardness Tester and in England by Sheen Ltd. A picture of the Sheen instrument is shown in Fig. 39.

To make a test, fasten the panel to a leveling table and adjust to a level position. Place the Rocker on the panel and set it in motion so that the bubble in the left hand tube travels slightly beyond the mark on the tube. Start to count swings when the bubble just fails to travel beyond the mark. Begin with zero. Stop the count when the bubble in the right hand tube fails to travel beyond its mark. The number of swings multiplied by 2 is the Rocker value. Alternately, the sum of the two successive determinations may be used.

To calibrate the Rocker, adjust the angle of the left hand tube to about 22.5° with the horizontal and that of the right hand tube to about 16°. Place the Rocker on a level sheet of polished plate glass and proceed as directed above. When in correct adjustment, the Rocker swings 50 times in 60 ± 0.5 s.

If 50 swings are not obtained, minor adjustments may be made by means of the weight on the vertical screw. Lowering the weight increases the number of, and at the same time, accelerates the speed of the swings. Major adjustments may be made by changing the angles of the tubes. Changing the angle of the right tube has a greater effect than an equal change in that of the left tube.

By widening the angle between the two tubes, the number of swings can be increased to one hundred or more, thus increasing the sensitivity. However, at wide amplitudes, the swings become somewhat more violent and too much should not be attempted in this direction. The rockers should be wiped off frequently with soft paper or a clean cloth. Solvent should be used, if needed.

In using the Rocker or the pendulums, it is essential that the film support be firm. Any movement absorbs energy and lowers apparent hardness. Thin panels may bend; warped panels may rock. To eliminate this source of error, H. F. Payne designed a holder, called the Cyanamid Holder. It is essentially a small screwpress. It eliminates slight curvatures and holds panels firmly. It takes panels up to 6 in. (15 cm) in width.

Films on heavy gage metal with a plane surface or films on plate glass or other rigid material may be supported on lumps of stiff putty or molding clay.

Another aid to proper use of the Rocker is a shield to protect it from air currents. One such shield is shown in Fig. 40.

Moore [*67*] studied the reproducibility of Sward rocker hardness measurements and found that a single measurement came within one unit of the average seven out of ten times. A deviation of more than two units appeared no more than 8 out of 100 times. Boscoe [*68*] explored the influence of atmospheric pressure and compared Sward rocker hardness with that obtained using other methods. He found that the greatest differences were due to differences between individual Sward rockers. This was also observed by Nielson [*69*], and Baker et al. [*70*] did a study on variations in results due to subjective differences in observers making the measurements. Pierce et al. [*60*] also studied various factors which influence the value of Sward hardness such as temperature, humidity, film thickness, substrate, and air pressure.

On analysis of the papers by Baker, Elleman, and McKelvie [*70*] and Pierce, Holsworth, and Boerio [*60*], a possible explanation of why ASTM Subcommittee D01.23 and Task Group D01.23.14 had difficulty with the data became apparent. They may have overlooked the information (Table 5) that two out of three Sward rockers were outside the proposed mass specification, 100 ± 10 g, proposed for D 2134, Test Method for Determining the Hardness of Organic Coatings with a Sward-Type Hardness Rocker.

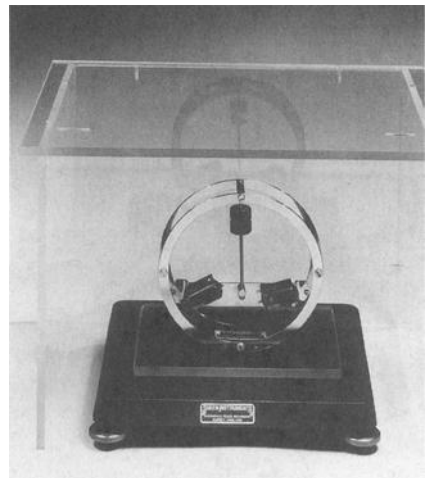

FIG. 39–Sward-Type Rocker Hardness Tester by Sheen, Ltd. (Courtesy of The Paul N. Gardner Company, Inc.)

Baker, Elleman, and McKelvie used the equations from Parker and Siddle and Persoz to derive the following formula to calculate the number of Sward rocker rocks (N)

$$N = \frac{tb}{2\pi} = \frac{1}{2\pi\gamma}\log\frac{(\theta_0 + \varphi)}{(\theta_n + \varphi)} \cdot \sqrt{\frac{Mga}{I} - \gamma^2} \qquad (13)$$

where

a = distance of center of gravity from instantaneous center,
θ = angle between the vertical and the plane containing the instantaneous center of rotation and the mass center,
θ_0 = initial amplitude of the rocker, and
θ_n = amplitude of the rocker after N rocks.

Mathematical analysis of pendulums, balls, and rockers, have been made by B. Persoz [*59*], Baker et al. [*70*], D. G. Flom [*71*], and P. E. Pierce et al. [*60*]. Persoz developed the relatively heavy (500-g) pendulum shown in Fig. 35. Baker et al. found that heavy rockers with a high moment of inertia appeared to give the best results. Flom investigated the relation of rolling friction to the dynamic shear modulus for polymers and emphasized the importance of elastic hysteresis losses in rolling friction (not to mention the viscous damping effect). They demonstrated that, for the case of a rigid sphere rolling on a viscoelastic surface, the following relationship existed

$$\mu = K \tan\delta\,(W/Ga^2)^{1/3} \qquad (14)$$

where

μ = coefficient of rolling friction,
$\tan\delta$ = dynamic loss tangent,
G = shear modulus,

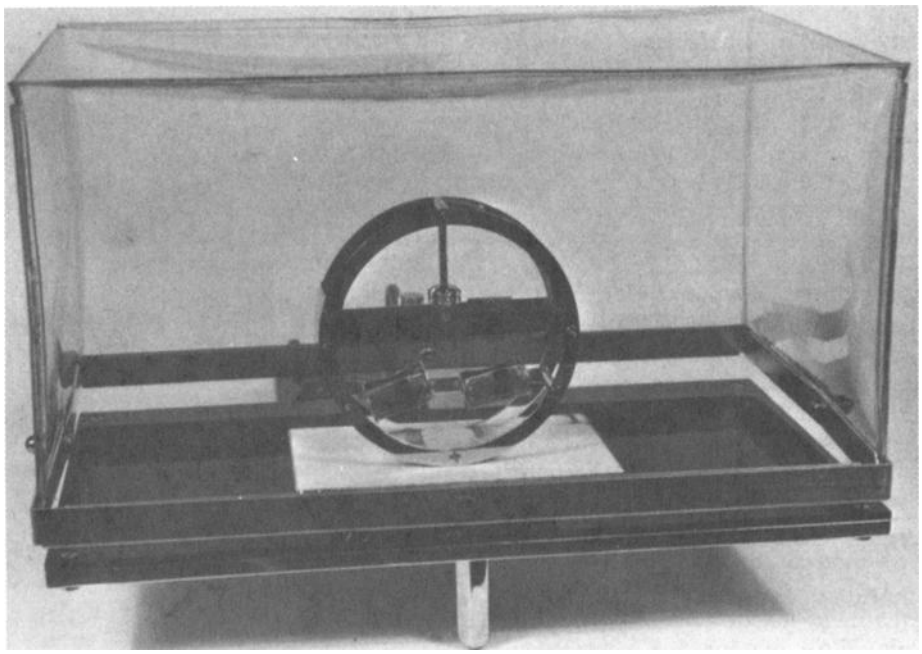

Fig. 40–Sward Rocker with shield for protection from draft.

TABLE 5—Comparison of Sward rockers.

Dimension	Rocker Number 1	2	3
Value of a (cm)	0.896	0.400	1.175
Moment of inertia I about center of gravity (cm·g^2)	2085	1616	1829
Period, T (s)	1.093	2.10	0.95
Mass, M (g)	114.2	87.4	105.4
Radius, r (cm)	5.075	5.075	5.075
Value of θ_0	44°	42°	43°
Value of θ_n	27°	27°	27°

a = sphere radius,
W = load, and
K = a constant.

For the Sward rocker, a and W are constant and Eq 14 becomes

$$\mu = K'G^{-1/3}\tan\delta \tag{15}$$

Pierce et al. showed, among other things, that the coefficient of rolling friction was inversely proportional to the Sward rocker hardness number, N. This can be expressed as

$$\mu \propto 1/N \tag{16}$$

Substituting this in Eq 16 and rearranging gives

$$G^{1/3} = NK''\tan\delta \tag{17}$$

In a plot of Sward rocker hardness against $G^{1/3}/\tan\delta \times 10^{-4}$, a linear relationship was found for hardness up to about 60; but for harder films, the plot curved and asymptotically approached a value of 100. This indicated that the Sward rocker was optimized for the range of hardness below 50, which corresponds to the range of hardness most frequently encountered with organic coatings. R. A. Cass [*71*] compared the Sward rocker hardness with the (tensile) elastic modulus of vinyl acetate copolymer coatings working in a range of film thickness from 1.2 to 125 mils. At constant film thickness he found the following relation between the hardness, N, and the elastic modulus, E

$$E = KN^3 \tag{18}$$

If we assume that E is very nearly the same as G, although it is well known that $E \cong 3\ G$ or less but not unity, substituting into Eq 18 and rearranging gives

$$G^{1/3} = NK' \tag{19}$$

which, according to Pierce et al., is the same as Eq 17 if we assume that $\tan\delta$ for the series of films studied is approximately the same. Cass went further in his analysis and arrived at the final equation

$$E = K_tN^3/t^3 \tag{20}$$

where

E = elastic modulus,
K_t = constant for varying thickness,
N = Sward rocker hardness number, and
t = film thickness.

However, by examining Cass' data we are able to go one step further, because the data show

$$K_t = 39t^{3.54} \tag{21}$$

hence

$$E = 39N^3t^{0.54} \tag{22}$$

showing, as was stated earlier, that the Sward rocker hardness is related to, or is a measure of, the modulus (stiffness) of a material as a function of its thickness. However, this is true only within certain limitations—the film must be thick enough and the substrate hard enough so that only the film properties are being measured.

Pierce et al. found hardness to increase as film thickness decreased to less than a few mils (their data were very limited). They also showed that softer substrates yielded lower hardness values for identical coatings, which simply means that the organic coatings were not thick enough for the measured hardness to be uninfluenced by the substrate. It is also obvious that the hardness value measured using a Sward rocker can be influenced by a "skin effect," or hard outer surface, while the bulk of the film is relatively soft.

Uses of the Sward Rocker—It is redundant to state that the Sward rocker is known and used all over the world. Canadian Government Specification Board standardized it in Method 116.2, Hardness, in Canadian Government Specifications 1-GP-71, Methods of Testing Paints and Pigments. We have seen that it can measure the coefficient of rolling friction and, within certain limits, measure the dynamic mechanical properties such as shear modulus or compliance of materials.

In addition to these it has been specified in ASTM Method D 2134. Softening may be encountered when a plasticized material comes into contact with an organic coating. However with regard to softening by plasticizers, it has been observed in the author's laboratory that, in some instances, the indentation hardness of the coating is unaffected, while the Sward rocker hardness decreases. This is due to an almost invisible film of plasticizer that has exuded out onto the surface of the coating, thereby acting to dampen the oscillations of the rocker.

BYK-Gardner, Inc. has distributed a graph which compares König hardness values with Sward Rocker hardness values and Persoz hardness values with Sward Rocker hardness values. These graphs are shown in Fig. 41 and Fig. 42.

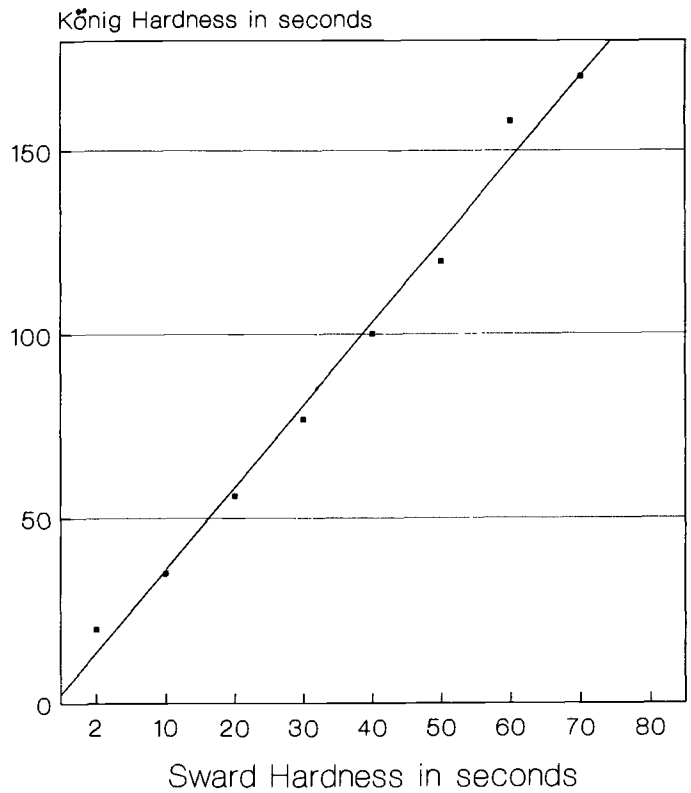

FIG. 41–Comparison of König hardness values with Sward Rocker hardness values.

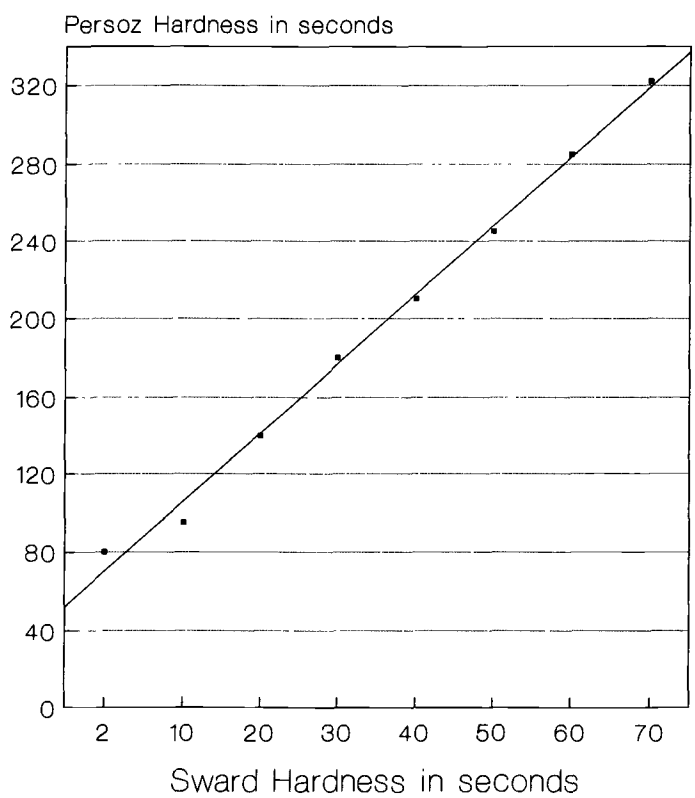

FIG. 42–Comparison of Persoz hardness values with Sward Rocker hardness values.

Rebound Hardness Testing

The rebound hardness test measures the mechanical properties of a material during very short time intervals. The test, which uses very simple apparatus, is performed by dropping an elastic steel ball from an initial height h_0 onto a flat test surface. The rebound height h_1 of the ball is measured. The impact resilience or hardness of the sample is the ratio of the rebound height to the initial height. The impact process occurs over a very short time interval (10^{-3} to 10^{-4} s) [*72*]. The resilience R is related to the loss tangent of the material [*73-75*].

$$R = h_1/h_0 = \exp(-\pi \tan\delta) \tag{23}$$

This loss tangent applies to a very fast impact process.

The results depend on geometric factors such as the thickness of the plate and the radius of the ball [*75*], as well as on the coating thickness and hardness of the substrate. Hard substrates, such as window glass, give good test results. The test has been used in a number of investigations of coatings [*46,76*]. A more elaborate form of the rebound apparatus has been developed by Raphael and Armeniades [*77*]. Their ADL Rebound Tester has provision for temperature control and can operate from liquid-nitrogen temperatures to several hundred degrees centigrade.

ADL Ball Rebound Apparatus—The ADL Ball Rebound Hardness Test Apparatus, developed by Arthur D. Little, Inc.'s M. Gordon and B. Grievenson [*78*] consists essentially

of a penetrometer and a brass block containing a heating element enclosed in a glass dome that can be subjected to a vacuum. The brass block can be heated from 0 to 300°C at rates of up to 30°C per minute. The specimen block can be cooled very quickly by sucking a stream of cold CO_2 gas through a side arm straight upon the specimen disk. The polymer film to be tested is mounted on the brass block, which has a circular perforation through which the ball hits the specimen disk. The mounted specimen is placed inside the glass dome, which can be evacuated or filled with an inert gas. The test ball (⅛ in. steel ball bearing) is released electromagnetically from the top of the dome. The rebound height is measured against an illuminated scale at the back of the dome. The rate of testing (i.e., the interval between successive ball rebounds) may be adjusted from 3 to 10 s per test. A similar apparatus was used by Jenckel and Klein [79] investigation of the relationship between ball rebound energy absorption and temperature in polymers.

Shore Scleroscope—Shore scleroscopes, developed by Shore [*35*], have been manufactured since 1907 as the pioneer American standard for testing the hardness of metals and other materials. They consist of a calibrated glass tube with a diamond-tipped metal "impactor" located inside. The hardness is measured by the height that the impactor rebounds. This instrument is available in various models depending upon the application. They are used to determine the hardness of thick elastomers, but results are greatly influenced by the substrate when thin polymers are tested. The American Bowling Congress (ABC) specifies a Scleroscope hardness for coatings used on bowling pins. However, the hardness of the thin clear coating is insignificant when compared to the plastic substrate and maple wood core.

PHYSICAL CONCEPTS OF MAR RESISTANCE TESTING

The mar resistance of an organic coating is its ability to withstand scratching, scuffing, and/or denting actions, which tend to disfigure or mar (change) the surface appearance of the coating. Mar resistance, as defined above, is a resistance of the surface of the coating to permanent deformation, as a consequence of the application of *dynamic* mechanical forces. In this sense it is distinguished from print resistance, pressure mottling, and block resistance, in which the applied mechanical forces are static. Some examples of potential marring of organic coatings are: sliding an ash tray or other object across a desk or other item of furniture, rubbing one's belt buckle, zipper, or buttons along the organic coating on an automobile as it is being washed, a child sliding a toy or other object along a wall, refrigerator door, etc., and a woman dragging a wash basket full of wet clothes off the top of a washer or dryer.

When we refer to the scratching associated with marring, we are really referring to relatively fine surface scratches. This distinguishes the type of scratch encountered in mar testing from that encountered when attempting to evaluate hardness or adhesion by means of various types of scratch tests. There are, in general, three different ways in which materials are scratched when being tested for mar resistance:

1. Single scratches made with a needle or other sharp instrument.
2. A large number of scratches made by abrasive particles falling or impinging on the specimen.
3. A large number of fine scratches made by an abrasive medium being rubbed against the specimen, called scuffing.

In No. 2 and No. 3, the results are similar in that there is a loss of gloss or a haze produced on the surface of the specimen being tested. Also, the abrasive medium in No. 3 may not be an abrasive per se, but can be a type of fabric.

Regarding single scratches made with a needle or other sharp instrument, two schools of thought have existed as to exactly what constitutes a mar. One school of thought considers the end point to be any marring, whether a depression or a scratch. The other school considers a mar to have occurred only if, within the scratch depression itself, skin rupture of the organic finish has occurred as evidenced by light scattering. This skin rupture is gaining wider acceptance, because it can be quantified or measured and given a number. Also, the skin rupture mechanism, as evidenced by light scattering, is identical to that encountered in No. 2 and No. 3.

Finally, there is another type of mar that has not been mentioned yet, because it does not fit into the definition expressed at the beginning of this section on mar resistance. This is the streaking or marking mar wherein the organic coating itself is not necessarily physically damaged, but it has been marked or streaked by a transfer of material to the coating. The most common example of this occurs when a coin, such as a nickel, is rubbed across the coating. If the metal is transferred to (streaks) the coating, the coating is said to be marred. This same mechanism occurs when a fingernail is used. The acceptance or use of this type of marring or mar resistance seems to be losing ground to the scratching types, and, at the risk of being redundant, a test for it has been never quantified or standardized.

General Motors Corp.'s Engineering Standards Group wrote, in 1988, GM9150P, Resistance to Marring or Scuffing. In the test method a Bronzette Gem paper clip, No. 1, is allowed to traverse a coated panel with a weight of 750 g applied to it. The coated specimen is pulled towards the operator at a speed of approximately 37 mm/s. The coated specimen is then rotated 90° counterclockwise. This is then repeated until the four directions are completed. The panel is then examined for marring or scuffing. A satisfactory coatings shows no marring or scuffing. An unsatisfactory coatings shows marring or scuffing. Rejected specimens are reinspected after a minimum of 15 min to be certain that the marring is not superficial and does not disappear upon standing.

Ford Motor Co.'s Quality Laboratory and Chemical Engineering Group wrote, in 1973, BN 8-4, Resistance to Scuffing. In the test method, a Taber abraser is used to determine the resistance to scuffing of materials such as painted substrates, vinyl, genuine leather, and luggage compartment mats. A special scuffing head is used.

Single Scratch Methods

BTL Balanced Beam Mar Tester—This method [*80*] was developed in 1945 by R. J. Phair of the Bell Telephone Laboratories (BTL). The apparatus is shown in ASTM Method D

2197: Test Methods for Adhesion of Organic Coatings by Scrape Adhesion [*53*]. In mar testing, the rounded tool is replaced by a chromium-plated phonograph needle. The apparatus consists of a balanced beam to which is secured a platform for supporting weights, a rod at an angle of 45° which holds the scratching needle, and a sliding or movable table on which to support and move the specimen. Initial adjustments are performed to ensure that the apparatus is level and that the end of the needle is directly in line with the weight support rod.

The procedure differs from that employed in adhesion testing in that the panel is drawn toward rather than away from the operator. A 50-g minimum load with 50-g increment creases is used. The end point is reached when the upper surface of the paint film has been ruptured. A breakdown point is distinguished from depressions in the finish by holding the marred specimen nearly at eye level in flat lighting so that no highlight reflections are visible. The least weight required to make a line which shows a distinct whitish reflection from the subsurface of the finish, but not from the base, is the mar value. Care is taken to avoid reflections from the side walls of depressions in the finish which are not cut through.

The mar point can also be observed by inspecting the marks under a microscope of 80 to 100 power. The deepest section of a depression will scatter the light where marring has occurred if it is illuminated along its length and at an angle of about 20° from the plane of the specimen. The appearance of a depression mark without marring is illustrated. Mar values of 200 g or more are usually indicative of sufficient resistance to withstand the scarring actions encountered in normal assembly of telephone apparatus.

In making a determination, the specimen is placed on the movable table with a starting load of 50 g on the weight platform. The needle is lowered slowly onto the specimen, with the end of the apparatus nearest the needle being directly in front of the operator. The movable table is pulled toward the operator with a slow, steady motion, at a rate of 1 to 1½ in. (25 to 38 mm)/s, for a distance of at least 3 in. (76 mm). At the end of each stroke the needle is raised off the specimen, and the specimen is moved slightly to the side. This procedure is repeated with a 50 g increase in load each time until the surface of the organic coating has been disrupted or ruptured.

Mar resistance is expressed as the load in grams required to rupture the surface of the coating as evidenced by light scattering. A mar or breakdown point is distinguished from depressions in the coating by holding the marred specimen nearly at eye level in flat lighting, so that no highlight reflections are visible. The least weight required to make a line that shows a distinct light scattering or whitish reflection in the depression made by the needle is the mar resistance value of the organic finish. Care must be taken to avoid reflections from the wall of depressions in the finish which are not cut through.

Years ago when telephone sets were made of metal, it was found that the baked black enamel used on the metal base of the desk type telephone would get through the numerous assembly operations in an unmarred condition if the value of mar resistance was 200 g or better. Materials having mar resistance levels of less than 200 g would not necessarily suffer damage to a degree sufficient to expose the base metal, but were rejected in many cases on the basis of unsatisfactory appearance.

ASTM Task Group D01.23.14 Hardness, Abrasion and Mar Resistance ran a preliminary round-robin test seeking a candidate apparatus around which they could write a test method. The results of the round-robin tests are shown in Table 6.

As a result of their findings, they wrote D 5178: Test Method for Mar Resistance of Organic Coatings [*53*] using the equipment R. Phair originally designed for adhesion testing. Several operators have expressed a lack of interest in this test method as the end point is difficult to recognize. Also a mark judged to be a mar may disappear overnight.

Princeton Scratch Tester—This apparatus is somewhat similar to the balanced beam tester, but instead of having a movable specimen table, the beam assembly itself moves on a V-shaped track, the specimen remaining immobile. Also, the needle is held at an angle of 90° to the surface of the specimen.

Hoffman Scratch Tester—This device, described in the section on hardness in this manual, has also been used to determine mar resistance. However, its use as a mar tester has never gained wide acceptance. The scratches obtained are usually quite large and often go down to the substrate.

Rondeau Scratch Tester—The same criteria that apply to the Hoffman scratch tester just mentioned also apply to the Rondeau Scratch Tester.

TABLE 6—ASTM Task Group D01.23.14 on hardness, abrasion and mar resistance. Results of round-robin tests on mar.

Sample/ Collaborator	Hardness (Pencil)				Eraser (Rubs)		Coin (Mar)		Erichsen (Swing)	Scrape Adhesion (Balanced Beam)[b]		RCA Tape Abrader
	1	2	3	4	1	4	1	4	5	2	3	4
No. 1 Zero	F/H	F	F	H	4	F	P	P	58	6	4	9 cycles
No. 2 Medium	H/2H	F	H	H	5	H	P	P	67	10	8	7 cycles
No. 3 Hi resis	H/2H	F	2H	2H	5	2H	P	P	62	>10.5	12	15 cycles
No. 4 Urethane	H/2H	F	2H	2H	4	HB	P	P	68	10.5	10	14 cycles
Orange lacquer	H/2H	F	2H	H	5	Slight	[a]Fair	P	90	10.0	12	55 cycles
No. 188	HB/H	HB	2H	B	3	Slight	[a]Fair	P	47	10.5	10	10 cycles

[a]Coin test (nickel) scratched the film but did not mar (metal marking) the surface.
[b]Grams, weight.

Impinging Abrasive Method

Falling abrasive particles are used as the principle in ASTM D 673: Test for Mar Resistance of Plastics [*81*]. This principle was also adopted as Method 1093: Mar Resistance, of Federal Test Method Standard No. 406. However, on 4 Jan. 1982, the Federal Government canceled this test method and replaced it with ASTM Test Method D 673. As indicated by the titles, the test was designed for but not limited to plastics. Therefore it can be used for testing mar resistance of organic coatings. It was developed by Boor in 1942 [*82*] and adopted as tentative by the ASTM in the same year. The test consists of allowing a measured stream of No. 80 carborundum particles to fall onto the specimen. Then, the degree of marring or mar resistance is evaluated by means of gloss measurements in accordance with ASTM D 1003: Test Method for Haze and Luminous Transmittance of Transparent Plastics [*81*]. It should be noted that, according to the U.S. Naval Ordnance Laboratory [*83*], the method is useful for both research and development and design criteria. A similar test was developed by the British in 1942 [*84*]. Instead of measuring the loss of gloss, the change in light transmission through the specimen was measured. Of course this restricted one to the use of transparent materials. Incidentally, it appears that G. G. Sward first suggested the loss of gloss of a surface by a definite amount of falling abrasive [*85*].

The apparatus consists of a hopper, motor, tube, support assembly, specimen holder, and the optical equipment required to measure the gloss and loss thereof. Uniform distribution of abrasive is obtained by rotation of the conical hopper at 7 rpm as abrasive flows through holes 0.070 in. (1.8 mm) in diameter. The abrasive flow rate is about 225 g/min. Usually, several abrasion tests with increasing amounts of abrasive are made, that is, 200, 400, 800, 1200, and 1600 g.

A special light projector and glossmeter are used to measure the gloss of the specimens. The following equation is used for calculating the percentage of gloss.

$$\text{gloss, percent} = 100\frac{I_1 - I_2}{I_1} \tag{24}$$

where

I_1 = photoelectric cell reading at the specular angle (45°), and

I_2 = photoelectric cell reading at the 60° angle (15° off specular).

The percentage gloss of the abraded or marred spots is plotted against the respective amounts of abrasive used to obtain a characteristic curve for each different material. Since such curves for different materials are often found to change slope irregularly, they may cross each other, and the rating of a series of different materials using a given amount of abrasive may not be representative of their relation at other amounts of abrasive. One way to arrive at an overall performance is to average the percentage of gloss at the various amounts of abrasive or the area under each curve.

In 1988, Committee D-20 stated in the Precision and Bias section of Test Method D 673: "a meaningful precision statement cannot be developed at this time because of the small number of laboratories presently known to be using this test method."

Scuffing Methods

Taber Abraser Mar Test—Use of the Taber Abraser for a mar test for polyester resins was studied by Sherr and Martin [*86*] employing ASTM D 1044: Resistance of Transparent Plastics to Surface Abrasion [*81*]. They measured the increase in haze (transmission) of abraded transparent plastics after 100 and 200 cycles/revolutions of the specimens. J. M. Carter[7] from U.S. Plywood Corp. modified this ASTM method so that it could be used to measure the mar resistance of organic coatings on opaque substrates. His method consisted of observing for the first visually perceptible mar, wear track, or change in gloss. The number of cycles required to cause such a change is expressed as the mar resistance of the coating. This method was used in some preliminary round-robin work in the mid-1960s.

The following procedure was adopted for a second round-robin test:

> *Mar resistance is* expressed as the number of abrasion cycles required to produce a visually perceptible mar, wear track, or change in gloss. The pair of CS-10F Calibrase wheels to be used shall be mounted on their respective flange holders, taking care not to handle them by their abrasive surfaces. The 1000 g loads shall be fixed to each side. The ST-11 stone shall be mounted fine side up or the ST-11 disk shall be mounted abrasive side up on the turntable and the wheels shall be refaced for 25 cycles, brushing the residue from the stone during the process. Adjust the suction pickup to just clear the surface of the track. The abrasive wheels shall be refaced after each test. CAUTION—Do not touch the surface of the wheels after they are refaced. The specimen shall be mounted on the specimen holder or turntable with the coating side up. Adjust the suction pickup to just clear the surface of the track. The Calibrase wheels and 1000 g loads shall be mounted as above. After each cycle or revolution of the specimen, stop the turntable and observe for the first perceptible sign of wear track starting to show. Observe by looking at an angle of 45° incident to the specimen with a light source in a line with and at right angles to the incident angle. A reading shall not be considered valid unless the mar includes at least 75 percent of the possible circumference of the wear track and as wide as the width of the Calibrase wheels.

In 1992, Task Group D01.23.14 Hardness, Mar and Abrasion Resistance initiated round-robin work using a test method developed by E. I. du Pont Co. for automotive finishes. The same Taber abraser used in Test Method D 673 is employed, but changes of gloss rather than transmitted haze are being measured.

Erichsen Scar-Resistance Tester—This instrument [*87*], shown in Fig. 43, is in frequent use throughout the world to measure coating surface damage. This device was designed to replace the traditional fingernail mar test. It contains a scarring tool in the form of a disc mounted on a screw and under pressure from a helical spring. The spring applies a force which is adjustable of 0 to 20 N. The instrument is placed onto the surface so that it rests on the two guide wheels and the marking wheel, which is locked then presses onto the surface with the preset force from the spring. The scar resist-

[7]Private communication between J. M. Carter and E. M. Corcoran.

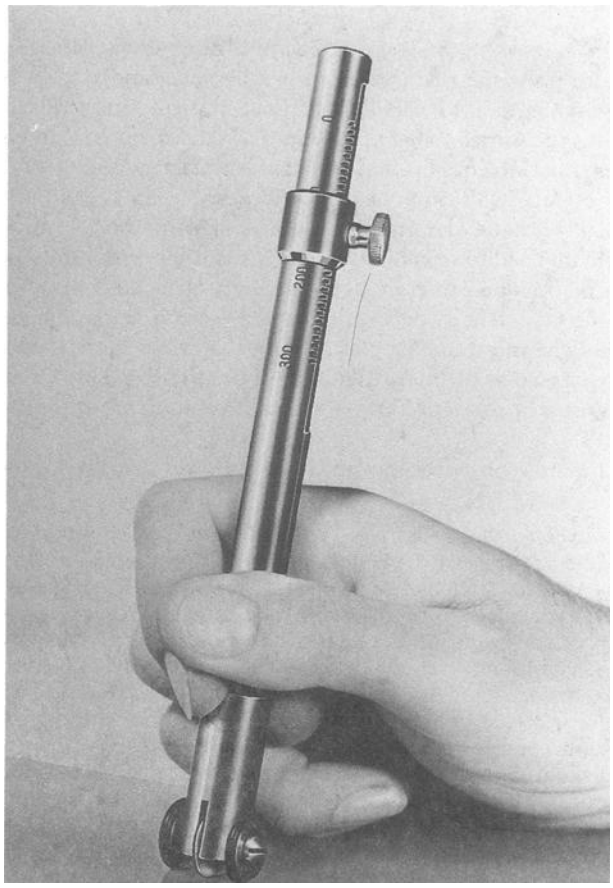

FIG. 43–Scar-Resistance Tester. (Courtesy of Erichsen GMBH & Co.)

ance result is the spring force at which the surface just shows a mark.

FDC Fine Scratch Test—The Furniture Development Council, London (FDC) designed a test in 1957 to determine the resistance of newly formed nitrocellulose lacquer films to damage when scratched, but it may be used on any type of coating. It consists of determining the loss of gloss of the organic coating when it is rubbed with a wool blanket.

A rubbing head with an area ¾ in. in diameter, under a load of 4 lb, is rotated on the specimen at 10 rpm for 2 min (20 rotations). The head is covered with No. 778, No. 3 Super White Blanketing from James Kenyon & Son, Ltd., made from 52/6S Good Quality English Wool, plain weave, 26 picks per inch, 32 ends per inch, 17½ ounces per square yard, scoured, and milled finish. Blanketing produces more scratches than most other common materials and is also more reproducible. A disk of blanketing may be used twice, once on each side.

Tests are made on films applied to two black glass plates. Five tests are made on each plate. A 45° gloss meter is standardized at 100 on an unscratched portion of the film, and the gloss of each scratched area is measured. For a difference in gloss to be considered significant, the difference in gloss between the marred and unmarred area must be greater than:

1. 1.7 for gloss of between 88 and 100, and
2. 2.7 for gloss below 88.

Miscellaneous Methods

Belt Buckle Test—At least as late as 1969, one of the major automotive companies used a belt buckle as one method of evaluating the mar resistance of the organic coatings on their automobiles. However, the exact method is not known to this writer.

Coefficient-of-Friction Mar Test—One of the leading manufacturers of mar resistance additives for organic coatings uses a sort of coefficient-of-friction test to evaluate mar resistance. This test consists of wrapping a 500-g weight in cheesecloth, placing the weight at one end of a test panel and slowly lifting the weighted end of the panel. The angle at which the weight slips off is taken as an indication of the coefficient of friction. The lower the angle, the better the mar resistance.

Coin Mar Test—A leading manufacturer of organic coating resins uses a nickel (five-cent piece) to evaluate the mar resistance of pigmented organic coatings. The manner or method that is used makes it a streaking or marking type of mar test. The test consists of dragging a nickel over a pigmented coating and seeing how much metal is transferred to the coating, as manifested by the size and color of the streak.

Fingernail Mar Test—Another leading manufacturer of mar resistance additives for organic coatings uses a fingernail to evaluate mar resistance. To make a test the back of a fingernail is dragged along the surface of the coating. If the coating is marked, it is considered to be marred. This is also a streaking or marking type of mar test. Others have used the edge of a fingernail in a similar manner.

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Stress Phenomena in Organic Coatings

by Dan Y. Perera[1]

INTEREST IN THE STRESS PHENOMENA in organic coatings is relatively new. The importance of understanding and measuring this stress became evident as facts accumulated about its role in coating degradation [*1–10*]. This is also supported by the fact that many coatings used today (e.g., thermosets) are more susceptible to developing high stresses than traditional ones (e.g., alkyd paints). It is now quite clear that stress can affect coating adhesion and/or cohesion and provoke delamination and/or cracking.

Since the development of stress is involved in practically all stages of coating life (film formation, exposure to various climatic conditions), its measurement is essential for a better understanding of coating behavior.

In addition, the measurement of stress can be used to evaluate other important characteristics of a coating, such as the glass transition temperature (Tg) and the critical pigment volume concentration (CPVC).

ORIGINS OF STRESS IN ORGANIC COATINGS

Stresses originate in organic coatings as a result of their adhesion to the substrate. Good adhesion is, on the one hand, indispensable for adequate substrate protection, but on the other hand prevents the normal movement of a coating.

The three main causes which provoke stress in an organic coating are [*11*]:

1. Film formation.
2. Variation in temperature.
3. Variation in relative humidity (RH).

The stresses induced by film formation, variation in temperature, and variation in RH are known, respectively, as internal, thermal, and hygroscopic. The latter two stresses are also referred to as hygrothermal (S^{HT}).

It is important to realize that, due to the coating adhesion to its substrate, stress exerts its action mainly in a plane parallel to the substrate [*6,12,13*]. Therefore, one can write

$$S = \frac{E\epsilon}{1 - \nu} \tag{1}$$

where

S = stress,
E = elastic modulus,
ϵ = strain, and
ν = Poisson's ratio.

Stresses are especially damaging at edges [*14*] where they cannot cancel each other or in the middle of the plate if defects or heterogeneities are present.

Film Formation

During film formation and regardless of the mechanism involved (evaporation of solvent, coalescence, chemical reaction, or their combination), in almost all cases the coating tends to contract. If this contraction is prevented by coating adhesion to its substrate and/or the mobility of macromolecular segments is hindered, a tensile stress will develop in the coating.

In the literature a certain confusion reigns about the denomination of the stress arising during film formation. For example, for solvent-based coatings an author may use these terms: cure stresses, solvent removal stresses, residual stresses, shrinkage stresses, internal stresses. For simplification, I suggest referring to the stress arising during film formation as internal stress (S^F).

If a liquid paint is applied on a substrate [*8*] and the development of stress is measured as a function of time, a number of stages can be observed (Fig. 1).

In Stage 0, the coating is still liquid and is mobile enough to permit volume contraction, and consequently no stress develops.

In Stage 1, the film starts to form, the volume contraction is restricted and stress develops.

In Stage 2, a number of processes can occur. Depending on the coating composition, the evolution of stress can include various combinations of increasing, decreasing, and stationary stress levels. If no damage occurs to the film (cracks, microfissures, loss of adhesion), a decrease in stress results from relaxation processes which occur from the moment the stress develops but only become evident at this stage. It also follows that the measured stress values are a result of two opposite processes, one tending to develop stresses in the coating (in this case due to the volume shrinkage) and the other tending to decrease them (due to stress relaxation).

Examples of stress development as a function of time for latex coatings [*15*] above and below the CPVC are shown in Fig. 2.

It is important to add that stress starts to develop in a coating when its Tg is at least equal to the experimental temperature [*6*]. For solvent-based coatings (Fig. 3), this is

[1]Head of Department, Coatings Research Institute (CoRI), Ave. P. Holoffe, B-1342 Limelette, Belgium.

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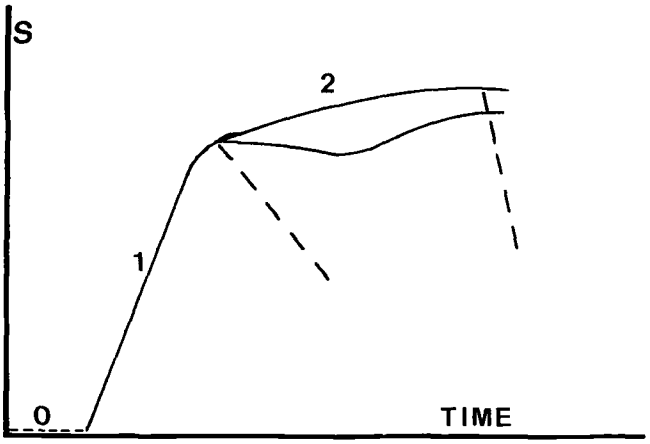

FIG. 1–Schematic description of stress (*S*) dependence on time.

also confirmed by the fact that stress appears when Phase 2 of the evaporation kinetics (the diffusion process) starts [*16*]. At this point in the evaporation, referred to as solidification, the solvent volume fractions are equal to the solvent concentration necessary to bring the Tg of the coating to a temperature equal or higher than the experimental one [*6,17*].

If Eq 1 is extended to accommodate the specific effect of internal strain, ϵ^F [*6*], then

$$\epsilon^F \simeq \frac{V_S - V_t}{3V_S} = \frac{\Delta V}{3V_S} \tag{2}$$

where

V_S = volume of coating at solidification, and
V_t = volume of coating at time t after solidification.

One can write [*18*] that

$$S^F = \int_{V_t}^{V_S} \frac{E}{1-\nu} \cdot \frac{1}{3V_S} dV \tag{3}$$

Despite the limitations of Eq 2, which assumes that the strain is isotropic and linear, Eqs 2 and 3 enable one not only to better understand the factors affecting the S^F but eventually to calculate it approximately.

Variation of Temperature

When coated substrates are exposed to variations in temperature, dimensional changes are induced. If the thermal expansion coefficients of the coating (α_F^T) and the substrate (α_S^T) are different, which is usually the case, a thermal stress (S^T) will develop in the coating [*2,7,11,19,20*].

Since the thermal strain, ϵ^T is given by

$$\epsilon^T \simeq (\alpha_F^T - \alpha_S^T)\,\Delta T \tag{4}$$

the combination of Eqs 1 and 4 gives

$$S^T = \int_{T_2}^{T_1} \frac{E}{1-\nu}(\alpha_F^T - \alpha_S^T)\,dT \tag{5}$$

Determination of Tg

A schematic description of the stress dependence on temperature [*18*] is represented in Fig. 4.

Such a dependence indicates the possibility of determining the Tg of a coating from the stress measurement. This is due to the fact that E, α_S^T, and ν (see Eqs 1 and 5) also show a profound change at Tg.

Below temperature *a* the coating is in the glassy region, and above temperature *b* the coating is in the rubbery region.

The linear dependence of S on temperature in the glassy region greatly facilitates the measurement of Tg. This linearity is due to the fact that in this region E, α_F^T, and ν are practically independent of temperature.

Three examples of the stress dependence on temperature and Tg determination by thermal stress measurements [*18*] are shown in Fig. 5.

When the stress magnitude in the rubbery region is small (e.g., elastomers, coatings with a low degree of cross-linking),

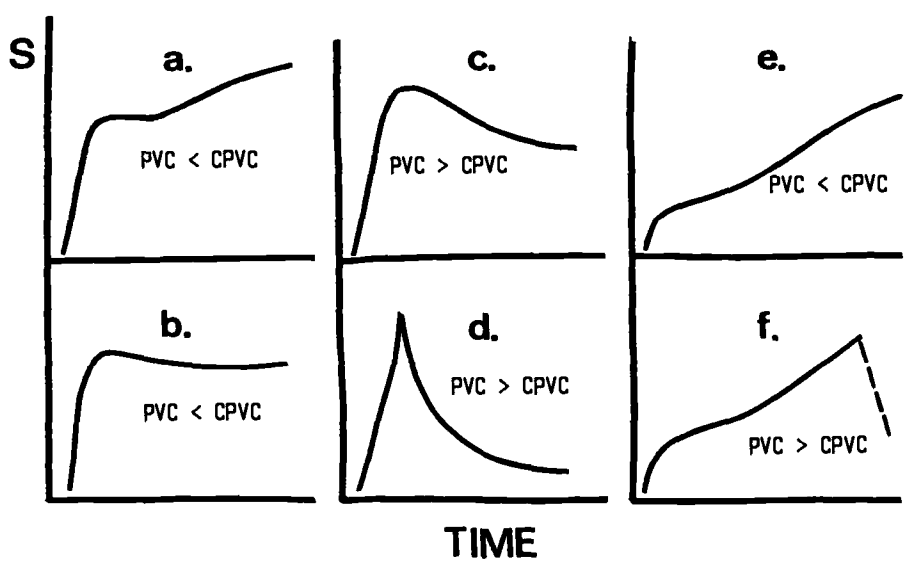

FIG. 2–Schematic description of stress (*S*) dependence on time for latex coatings [*15*]: (a) and (b) PVC < CPVC; (c) and (d) PVC > CPVC; (e) PVC < CPVC in the presence of a poor coalescent; (f) PVC > CPVC in the presence of a poor coalescent.

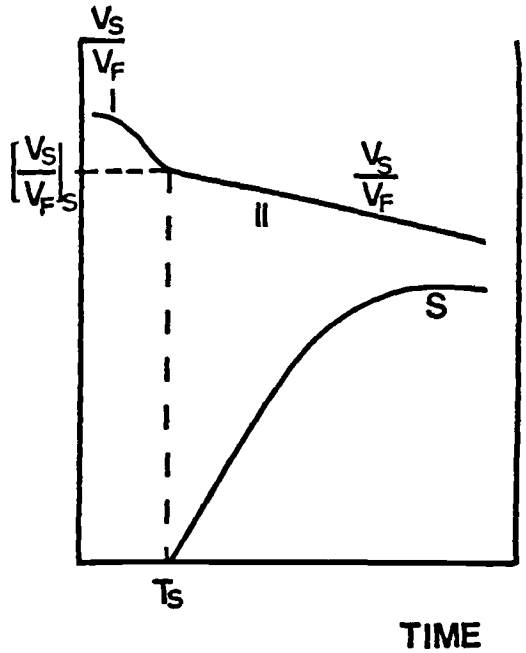

FIG. 3–Schematic representation of the dependence of V_S/V_F and stress (S) on time [*16*]. V_S = volume of solvent present in the film; V_F = volume of the dry film.

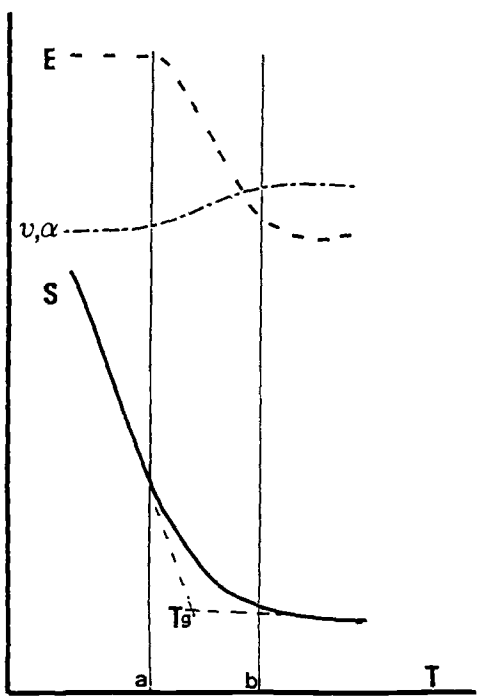

FIG. 4–Schematic representation of dependences of S, E, α_F^T, and ν on temperature (T) [*18*].

the Tg can be determined with fair accuracy just by carrying out a few measurements in the glassy region and then extrapolating the straight line to $S^T = 0$.

For coatings with a significant stress in the rubbery region (e.g., highly cross-linked thermosets), the measurement of stress in this region might provide a way to approximately determine the cross-link density, ν_e [*21*].

Since in accordance with the molecular theory of rubber elasticity in its simplified form [*22,23*]

$$E_r = 3\nu_e R T_r \tag{6}$$

and

$$S_r = 2E_r \epsilon_r \tag{7}$$

giving

$$\nu_e = \frac{E_r}{3RT_r} = \frac{S_r}{6RT_r\epsilon_r} \tag{8}$$

where R, S_r, E_r, and T_r are, respectively, the gas constant, the stress, the elastic modulus, and the temperature at the beginning of the rubbery region. If S_r is measured and ϵ_r is known or determined from separate measurements (e.g., by thermomechanical analysis, TMA), ν_e can be calculated.

Others have used the evaluation of Tg by stress measurements to investigate the effect of a pretreatment on certain pigments [*24*], the state of cure of baking enamels [*21*], and the modification of epoxy coatings [*19a,25*].

Variation of Relative Humidity

Dimensional changes induced by absorption and desorption of water as a result of variation in RH is another cause of stress development in a coating [*11,26,27*]. As in the case of temperature, if a mismatch between the expansion coefficients of the coating and the substrate exists, a hygroscopic stress (S^H) will arise in the coating.

Since the hygroscopic strain ϵ^H is given by

$$\epsilon^H \simeq (\alpha_F^H - \alpha_S^H)\,\Delta\,\mathrm{RH} \tag{9}$$

one can write that

$$S^H = \int_{\mathrm{RH}_1}^{\mathrm{RH}_2} \frac{E}{1-\nu}(\alpha_F^H - \alpha_S^H)\,d\,\mathrm{RH} \tag{10}$$

where α_F^H and α_S^H are, respectively, the hygroscopic expansion coefficients of the coating and the substrate.

Some examples of the S^H dependence on RH is given in Fig. 6.

INTERDEPENDENCE OF STRESSES

While in previous subchapters the various stresses (S^F, S^T, S^H) were discussed separately, in practice they can act together in such a way that the total stress (S_{tot}) is small or, as in many cases, very important [*11*]

$$S_{tot} = S^F \pm S^T \pm S^H \tag{11}$$

The positive and negative signs are arbitrarily chosen. The positive sign denotes a coating tendency to contract (tensile stress) and the negative sign a coating tendency to expand (compressive stress). S^F is practically always positive.

Equation 11 indicates the existance of two climatic conditions which might provoke a high stress in a coating:

1. Low temperatures and RH's induce high tensile stresses (e.g., a dry, cold winter).
2. High temperatures and RH's induce high compressive stresses (e.g., a humid, warm summer).

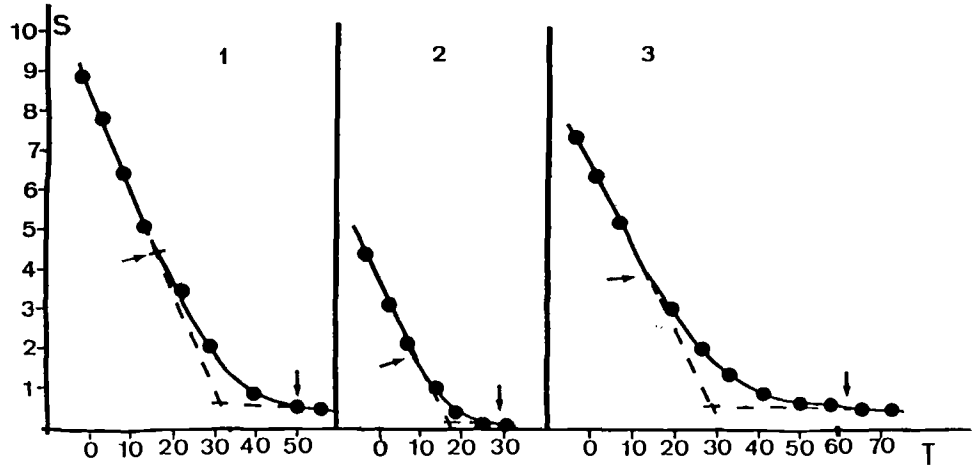

FIG. 5–Stress (*S*, MPa) dependence on temperature (*T*, °C) for three coatings at RH ≃ 0% [an epoxy (1), a polyurethane (2), and an epoxy/melamine system (3)] [*18*].

According to Eq 11 and depending on the type of coating and the way it was cured, a number of situations can arise. For example, for a thermosetting coating cured at a high temperature (i.e., at $T > \text{Tg}$, RH = 0%) and then exposed to different RH's, since $S^F \approx 0$, the S_{tot} is given by

$$S_{tot} = S^T - S^H \tag{12}$$

In Fig. 6, for one coating, the stress is positive regardless of RH, meaning that S^T is always higher than S^H; but cases where negative stress values are obtained are not rare.

It could be demonstrated [*11*] that the same coating conditioned in an identical environment but with different previous histories can develop different values of stress. Thus, a coating cured under isothermal and constant RH conditions (e.g., 21°C and 50%) will develop a total stress given by

$$S_{tot} = S^F - S^H \tag{13}$$

Now, if the coated substrate is first heated at $T > \text{Tg}$ for sufficient time to enable a maximum stress relaxation and then brought back to the initial conditions (i.e., 21°C and 50% RH)

$$S_{tot} = S^T - S^H \tag{14}$$

The results obtained [*11*] show that in certain cases (e.g., for an epoxy coating), the S_{tot} can be very different [S_{tot} (Eq 13) = 5 MPa; S_{tot} (Eq 14) = 0.4 MPa].

Interesting cases are those where the Tg of a coating is close to or below the experimental temperature once they are immersed in water or exposed to a high RH [*28*]. Under such conditions S^F or S^T can relax and therefore $S_{tot} = S^H$.

Such a situation is illustrated schematically in Fig. 7 and for a particular epoxy coating in Fig. 8.

Once a coated substrate is immersed in water one can observe first the development of a hygroscopic compressive stress followed by its decrease. The time necessary to reach zero stress is mainly dependent on the type of coating. The withdrawal of the coated substrate from water provokes first the development of a relatively high tensile hygroscopic stress followed by its decrease. The decrease in stress (Curves 2 and 4 in Fig. 7) is due to relaxation processes facilitated by the low Tg of the coating. The much higher stress values attained after the immediate withdrawal of the coated substrate from water (Curve 3 in Fig. 7), in comparison with the initial stress ($S_{tot} = S^F - S^H$ or $S_{tot} = S^T - S^H$) are due to the high hygroscopic tensile stress ($S_{tot} = S^H$).

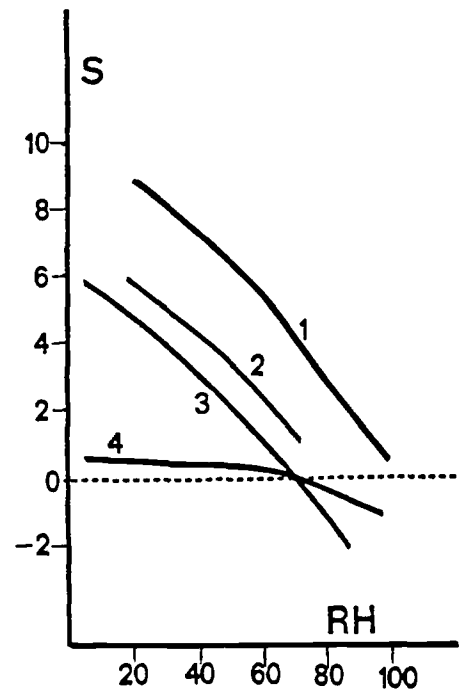

FIG. 6–Stress (*S*, MPa) dependence on relative humidity (RH, %) for a polyester powder coating (1); an epoxy (2); a polyurethane (3); and a latex coating (4) [*27*].

The above findings are important not only for understanding the mechanism of the stress development in organic coatings but also for practical reasons such as choosing the experimental conditions of natural or accelerated weathering tests, i.e., the magnitude of stress developed in a coating might depend as much on natural climatic conditions as on the type and order of cycle selected in the laboratory.

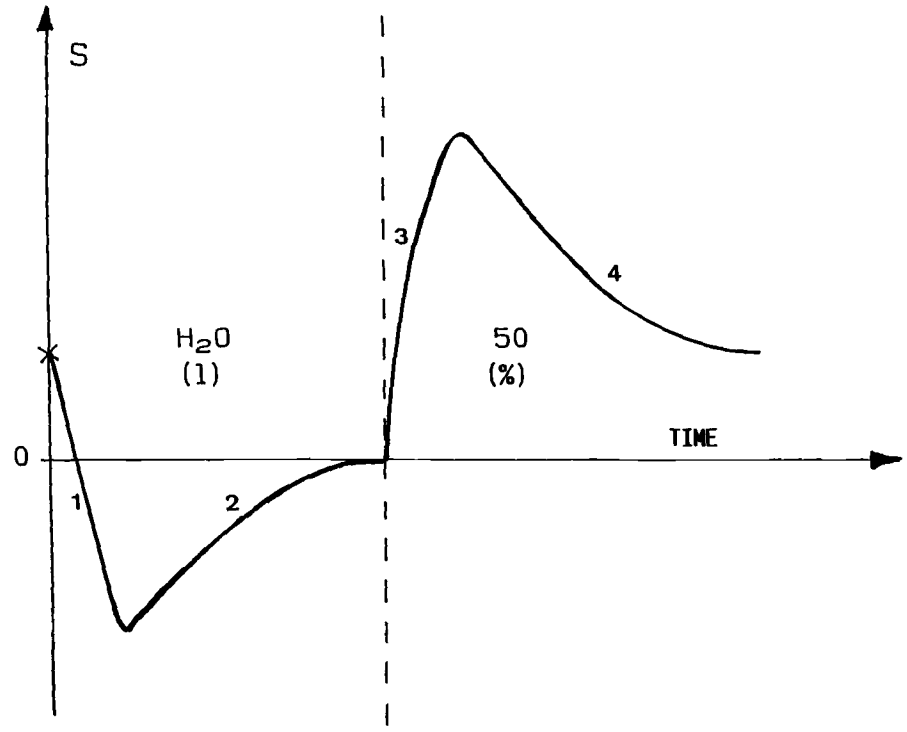

FIG. 7–Schematic description of the stress (*S*) dependence on time at two experimental conditions (water and 50% RH). *X* = the initial stress [*28*].

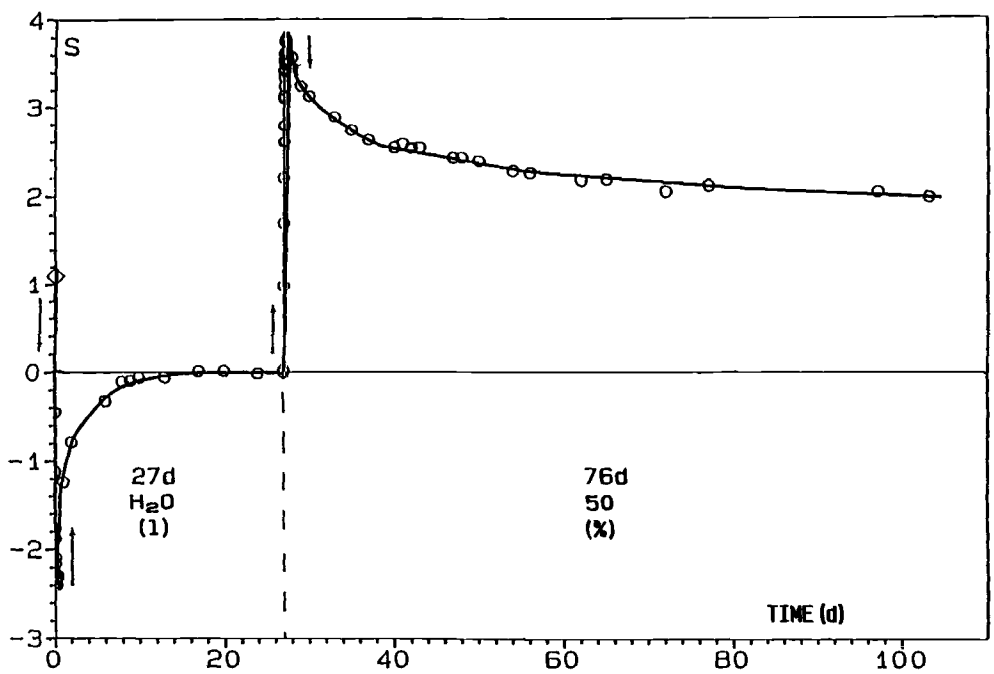

FIG. 8–Epoxy coating. Stress (*S*, MPa) dependence on time (*d*, day) at two experimental conditions (water and 50% RH); ◇ = initial stress [*28*].

STRESS MEASUREMENT

Equations 1, 3, 5, and 10 show that, if one knows the values of E, ϵ, and ν of a coating, then in principle the various stresses can be calculated. However, except for relatively simple cases, this is difficult because the above coating characteristics can be time, temperature, and relative humidity dependent.

Therefore, efforts were made to directly determine the stress arising in a coating. Among the methods one can find in the literature are: optical [*29–32*], strain gages [*19a,33,34*], brittle lacquer materials [*35*], X-ray diffraction [*36*], and cantilever (beam) [*2,4,8,11,26,37–43*].

The cantilever (beam) method appears to be the most widely used and is suitable for determining the stress in an organic coating. This method makes use of the fact that for a

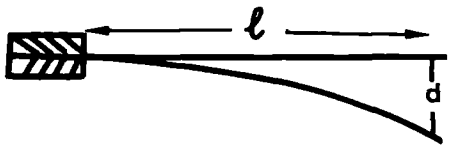

FIG. 9–Schematic description of the vertically fixed at one end cantilever (beam) method [*67*].

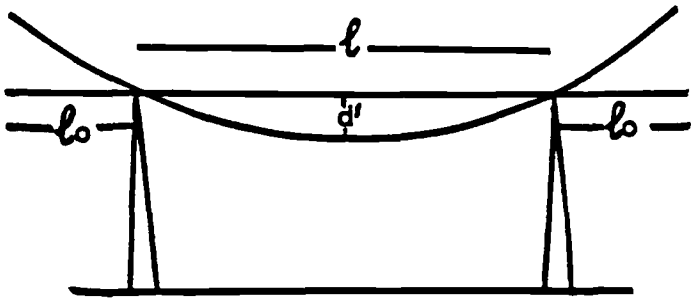

FIG. 10–Schematic description of the freely supported beam method [*67*].

coating under stress, applied on a substrate, the coated substrate will deflect in the direction which relieves the stress. Since the deflection can be measured and the elastic properties of the substrate are known from separate determinations, the stress can be calculated.

Two variations of the cantilever (beam) method are described in the literature: a one-sided coated substrate either (1) fixed vertically at one end [*4,8,26,37*] (Fig. 9) or (2) freely supported on two knife edges [*2,11,41,43*] (Fig. 10).

The stress analysis of (1) is more complicated and shows that to eliminate the effect of clamping on the coated substrate deflection, its measurement should be made at a distance higher than 80 mm from the clamping point [*8*]. Variation (2) is much simpler to analyze and can be designed to eliminate the effect of weight loss on the coated substrate deflection by choosing the right distance between the two knife edges [*43*].

Each variation has its advantages, but if correctly used they should give identical results. For example (1) is more suited to evaluating stress in water [*28*] and (2) to determine the effect of temperature [*2,11*].

Among the techniques used to measure the deflection of coated substrates, one can mention: capacitive transducers [*42,43*], laser [*44*], travelling microscope [*4,8,26*], automatic micrometer [*11*].

A commercial apparatus, the CoRI stressmeter (Fig. 11), is based on Variation (2) and the mathematical analysis described in Ref *43*. This apparatus is almost completely automatic and enables one to measure the stress from about −5 to 100°C under a variety of RH's.

A number of mathematical equations are proposed in the literature to calculate the stress, but in the author's opinion those proposed by Corcoran [*40*] are the closest to the real situation (e.g., considers the fact the stress develops in two directions)

$$S = \frac{dE_S t^3}{3l^2 c(t + c)(1 - \nu_S)} + \frac{dE(t + c)}{l^2(1 - \nu)} \tag{15}$$

$$S = \frac{4d' E_S t^3}{3l^2 c(t + c)(1 - \nu_S)} + \frac{4d' E(t + c)}{l^2(1 - \nu)} \tag{16}$$

where

d = deflection of the substrate (Fig. 9),
d' = deflection in the middle of substrate (Fig. 10),
E_S = elastic modulus of the substrate,

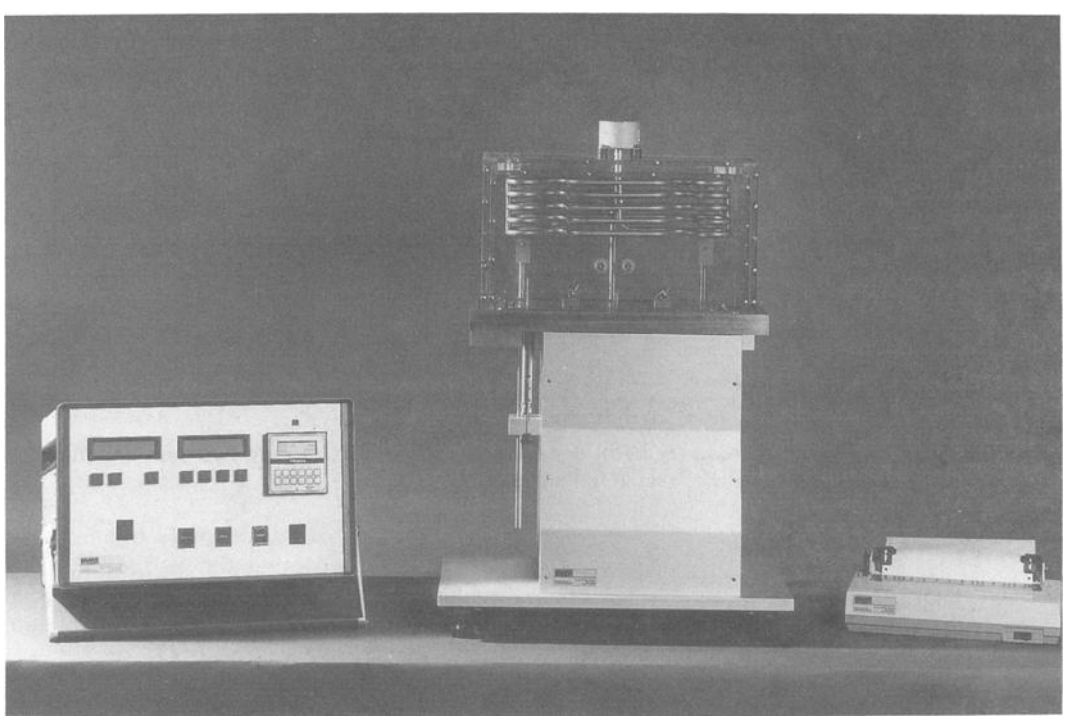

FIG. 11–CoRI stressmeter apparatus (Courtesy of Braive Instruments, Liege, Belgium).

ν_S = Poisson's ratio of the substrate,
t = thickness of the substrate,
c = thickness of the coating,
l(Eq 15) = length of the coated substrate between the point at which it is clamped and the point at which the deflection is measured (Fig. 9), and
l(Eq 16) = distance between the two knife edges (Fig. 10).

Equations 15 and 16 assume, among other things, good adhesion between the coating and the substrate, isotropic elastic properties of the coating and the substrate, the elastic limit of the substrate is not exceeded, and the stress is constant throughout the coating thickness.

The second term in Eqs 15 and 16, which contains a number of coating properties difficult to determine, can be neglected if $E_S \gg E$ and $t \gg c$.

Most commonly, stainless steel or cold laminated steel [*4,8,11,26,42,43*] shims are used. Other substrates such as aluminum can also be used.

The elastic modulus, E_S, of each shim can be determined prior to use with the CoRI stressmeter by applying Eq 17

$$E_S = \frac{Pl^3}{4d't^3b} \tag{17}$$

where

P = weight placed in the middle of the substrate,
b = width of the substrate, and
d', l, t = as in Eq 16.

It is important to add that, although it is not difficult to make the measurements, nevertheless great care is necessary. One should always use the correct substrate thickness, adequately condition it, and precisely calibrate the apparatus.

EFFECT OF COATING COMPONENTS

Since E, ϵ, and ν (Eqs 1, 3, 5, and 10) are known to be affected by the coating components, one should expect the same to hold for stress development. This section will briefly review the influence of pigmentation, solvents, and binder.

Pigmentation

It has been shown that pigmentation, both the pigment volume concentration (PVC) and the type of filler (i.e., pigments and extenders), affects the development of internal stress [*7,41,45–50*]. To illustrate this, examples are presented in Figs. 12 to 17.

Figures 12 and 13 show, respectively, the stress dependence on time for a thermoplastic binder in solution and a latex, filled with a titanium dioxide (TiO_2). Some PVCs are above the CPVC, and some are below the CPVC.

The different stages occurring during the film formation, discussed previously, can be recognized. In Stage 1 stress increases relatively rapidly. For latex coatings, this stage corresponds to the transition phase of the evaporation kinetics when the greatest part of the coalescence occurs. In Stage 2 (which corresponds to Phase 2 of evaporation kinetics), depending on the PVC and the type of filler, the stress can decrease or first decrease and then increase. For PVC < CPVC, this decrease is mostly due to the relaxation process, but for PVC > CPVC is mostly due to relief processes such as filler/binder dislocations and/or formation of microfissures.

Determination of the CPVC

The plot of the maximum internal stress (Sm) as a function of PVC enables one to determine the CPVC of a coating. Some examples are presented in Figs. 14 and 15.

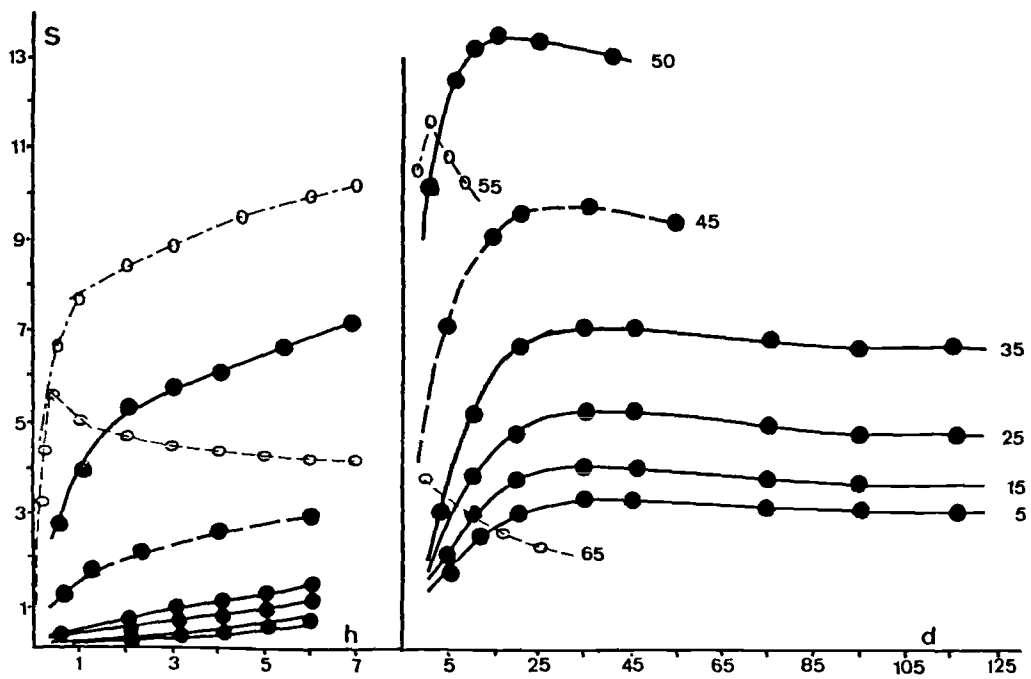

FIG. 12–Stress (*S*, MPa) as a function of time [hour (h) and day (d)] for a polyisobutyl methacrylate filled with TiO_2. The numbers in the figure indicate the different PVCs (%) investigated [*48*]. CPVC = 51%.

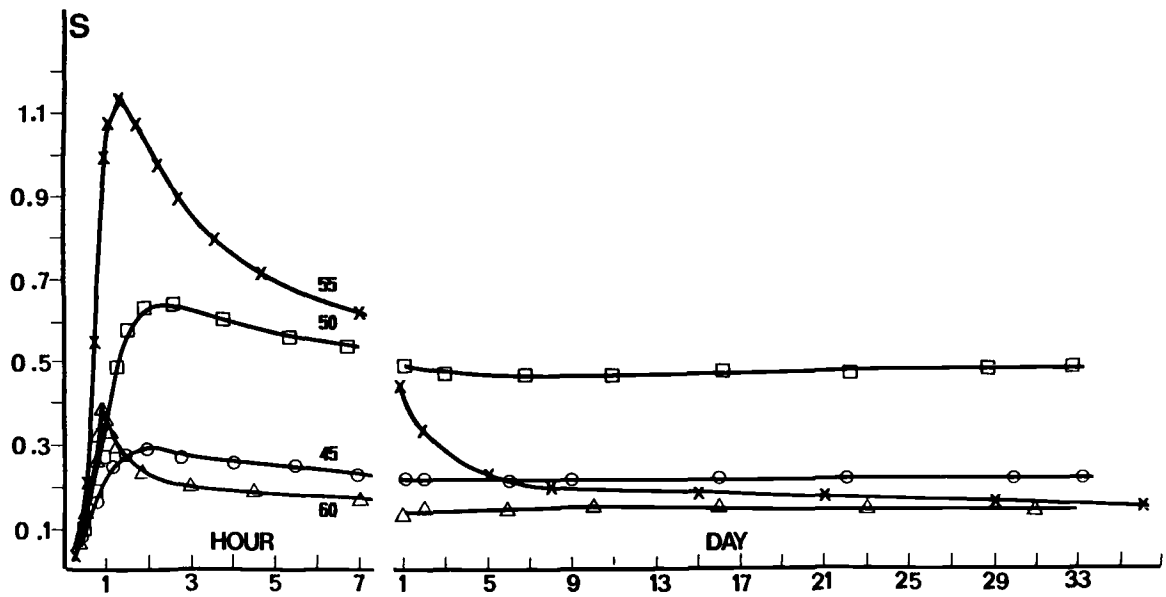

FIG. 13–Stress (*S*, MPa) as a function of time for a latex (vinyl acetate/vinyl versatate copolymer filled with TiO_2) [*50*]: 45% (○); 50% (□); 55% (X); 60(△). CPVC = 52%.

These figures, as well as other results presented in Refs *48* and *49*, clearly indicate that *Sm* is a function of PVC. *Sm* increases with PVC up to a certain PVC and then decreases. This PVC corresponds to the CPVC, indicating the possibility of accurately determining this characteristic [*51,52*] from stress measurements, and agrees well with the CPVCs calculated or determined by other methods (density, various mechanical properties).

The dependence of *Sm* on PVC can be understood if one considers Eq 1 and the way E, ϵ, and ν are affected by the PVC.

For PVC < CPVC, E increases with increasing PVC because the E of an inorganic filler is in general higher than that of an organic binder [*53*]. For PVC > CPVC, E decreases as a result of the increasing film discontinuity [*22,54*]. Since in general ϵ and ν are decreased (or are little affected) by the PVC, it follows that the increase of *Sm* with PVC is mainly due to the effect of PVC on E.

Figures 14 and 15 also show that the magnitude of *Sm* is dependent on the type of filler. There are fillers which induce a higher stress (e.g., TiO_2, red iron oxide) than others (e.g., $CaCO_3$, talc). This is due to the filler/binder interaction (reinforcing effect), which is determined by the nature and, in particular, by the surface area and the acid/base character of the binder [*55*].

Examples of $Sm = f(\text{PVC})$ for coatings containing a mixture of fillers are presented in Figs. 16 and 17.

An examination of the results obtained with binary and ternary filler coating systems indicates that the stress Sm_t can be calculated by means of an additive rule

$$Sm_t = n_1Sm_1 + n_2Sm_2 + \cdots + n_iSm_i = \sum_{x=1}^{x=i} n_xSm_x \quad (18)$$

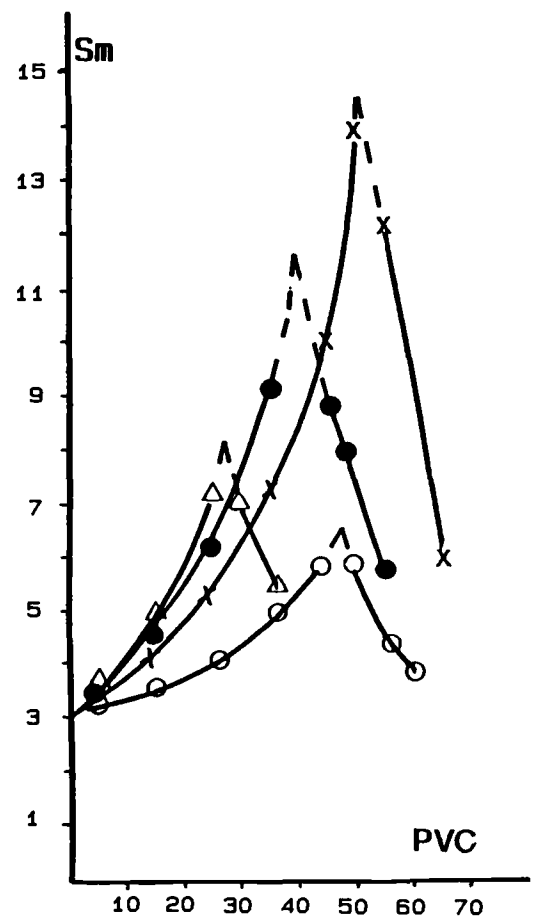

FIG. 14–Maximum internal stress (*Sm*, MPa) as a function of PVC (%) for a solvent-based thermoplastic binder filled with a TiO_2 (X), a red iron oxide (●), a yellow iron oxide (△), and a talc (○) [*48*].

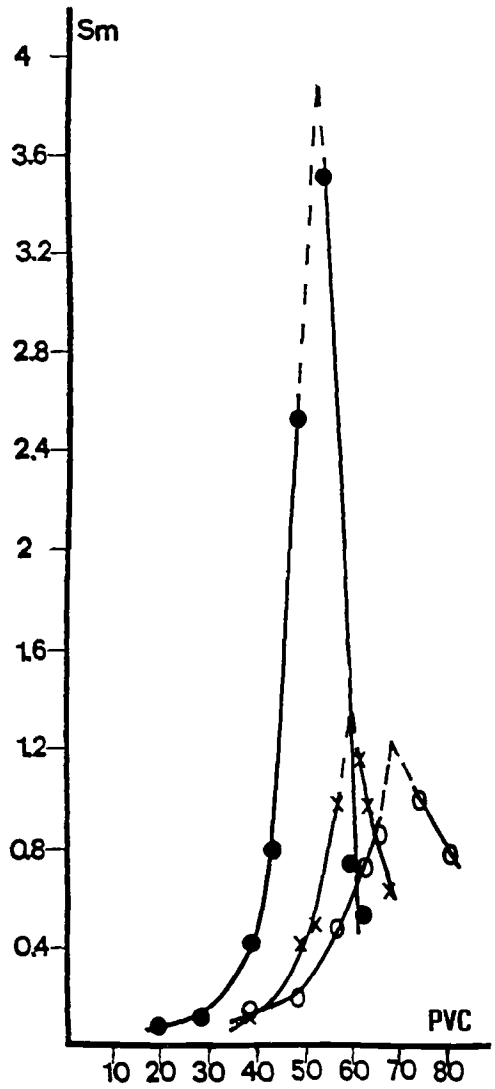

FIG. 15–*Sm* (MPa) as a function of PVC (%) for a styrene acrylic copolymer filled with a TiO_2 (●), a calcium carbonate (X), and talc (○) [*49*].

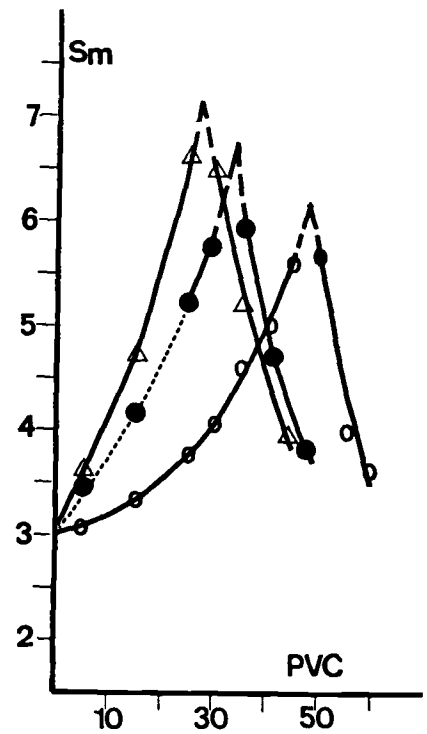

FIG. 16–*Sm* (MPa) as a function of PVC (%) for a thermoplastic binder in solution containing a yellow iron oxide (△), a talc (○), and their mixture (n = 0.5) (●); n = pigment volume fraction [*67*].

where

n_1, n_2, n_i = volume fraction of different fillers present in the mixtures, and

Sm_1, Sm_2, Sm_i = maximum stress of different single filler systems at a given Λ below or equal to 1 (Λ = reduced PVC, PVC/CPVC).

In the literature one can also find simplified methods to determine the CPVC of latex coatings based on the same principle. They simply compare the force [*56*] or the deflection induced by the internal stress for flexible plastic substrates [*57*] (Fig. 18) coated with paints of different PVCs.

These methods can be useful, but one has to be aware that they are valid only if both the thickness of the various paints and the time necessary to reach the maximum stress are the same.

Solvents

The presence of solvents in a coating can affect the magnitude and especially the rate of development of internal stress. This is illustrated in Fig. 19.

For thermoplastic binders in solution, the slower the evaporation of a solvent from a coating, the slower the development of internal stress and vice versa. One should note that the coating cast from fast-evaporating solvents (Curve 1, Fig. 19) produces slightly higher stress values than those cast from more slowly evaporating ones (Curves 3 and 4, Fig. 19).

The results obtained were explained by using Eq 1, the principle of plasticizing effectiveness of solvents and the stress relaxation favored by the presence in the coating of the slower evaporating solvent [*16*].

For coatings containing a mixture of solvents (Fig. 20), both the development rate and the stress magnitude are mainly determined by the presence in the film of the less volatile solvent(s).

The situation may be different if the film formation is a result of solvent evaporation and cross-linking processes (e.g., epoxy and polyurethane coatings). Under such circumstances the coating containing faster evaporating solvents can develop smaller stress values [*58*]. For such coatings, the volume of solvent present in the film after most of the cross-linking has occurred (Eq 2) and which determines the magnitude of ϵ^F will increase the slower the solvent evaporates. If the stress relaxation process is negligible, it follows that for

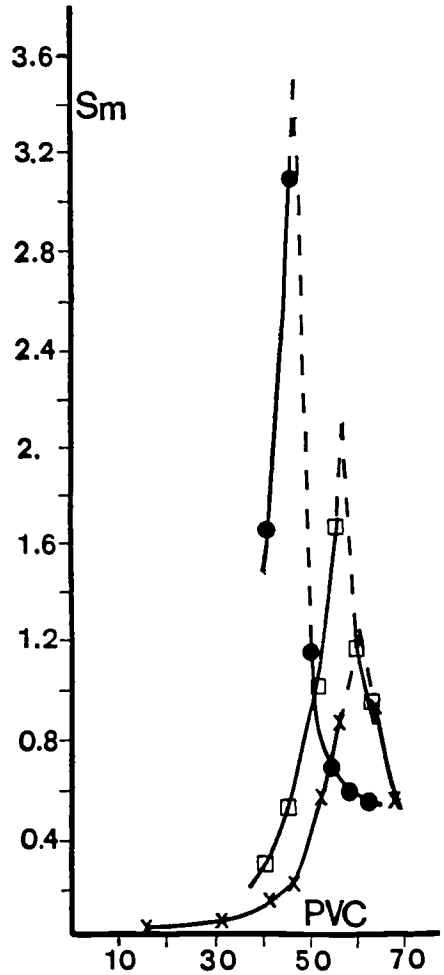

FIG. 17–*Sm* (MPa) as a function of PVC (%) for a latex binder containing a TiO_2 (●), calcium carbonate (X), and their mixture: TiO_2 (n = 0.4)/$CaCl_3$ (n = 0.6) (□) [*49*].

such coating systems the faster the solvent evaporates the smaller the internal stress.

The influence of solvents on internal stress is also evident for latex coatings where certain solvents, for example the coalescents, play an important role in the film formation process [*15,50,59*].

Examples of how the level and the type of coalescent affect internal stress are presented in Figs. 21 and 22, respectively.

Figure 21 shows that: (1) the coalescent level affects the time necessary to reach the maximum stress, and (2) for each formulation, there is an optimal coalescent level to obtain a tight continuous coating developing the lowest internal stress.

In Fig. 22, the results obtained with three solvents used in latex coatings are given. One can see that the type of solvent influences both the value and the development rate of the internal stress.

As in the case of thermoplastic coatings, the influence of solvents on internal stress development in latex coatings was explained [*15,50,59*] by taking into consideration the plasticizing effectiveness [*17,60*], the molar volume, and the steric hindrance of solvents. The plasticizing effectiveness affects the internal stress magnitude, while the molecular dimensions affect the evaporation kinetics and consequently the rate of the stress development.

Binder

To understand the role of the binder, the essential component of an organic coating on stress development, one can consider once again the general Eq 1 (see also Eqs 3, 5, and 10) and/or the Tg of a coating with respect to the experimental temperature.

Equation 1 indicates that the stress is directly affected by the magnitude of E, ϵ, and ν of the binder. The smaller the values of E, ϵ, and ν, the smaller the magnitude of stress.

With respect to the Tg, it should be remembered that the binders having their Tg below or close to the film formation temperature (T) develop a negligible internal stress, while those having their Tg $> T$ develop an important one. This is due to the fact that at $T >$ Tg, the mobility of the binder molecular segments is high and the stress arising during film formation can partially or totally relax. Moreover, it can be shown that for a thermoplastic binder in solution having a Tg $> T$, the lower the Tg of the binder, the less will be the solvent in the film after its formation (see Eqs 2 and 3) and therefore the smaller the internal strain and stress in the dry coating [*16*].

In brief, any change occurring in the molecular structure of a binder (e.g., crosslinking, crystallinity, molecular weight, steric hindrance) might induce a change in E, ϵ, ν, and Tg and thus affect stress development.

STRESS VERSUS ADHESION AND COHESION

It is accepted that the stress arising in a coating can reduce the adhesion and cohesion, two crucial properties of an organic coating for obtaining durable coatings [*1–10,61–65*].

The way the stress affects adhesion is described in detail in Refs *61* and *62*. It is shown that the application of an energy balance analysis [*66*] leads to the factor β acting against adhesion

$$\beta = cU_r \approx c\frac{E\epsilon^2}{1-\nu} \tag{19}$$

where U_r is the recoverable strain energy.

Because it is the energy that expresses the effect of ϵ, tensile or compressive strains are identical in their effect [*61*].

To accommodate the effect of stress [*18,27,67*], Eqs 1 and 19 are combined

$$\beta \approx cS\epsilon \tag{20}$$

Equation 20 indicates that adhesion is directly affected by c, S, and ϵ and the larger their values the higher the tendency of the coating to detach from its substrate. Thus, if a high stress arises in a coating, in order to prevent its detachment, it should be applied in a thinner layer.

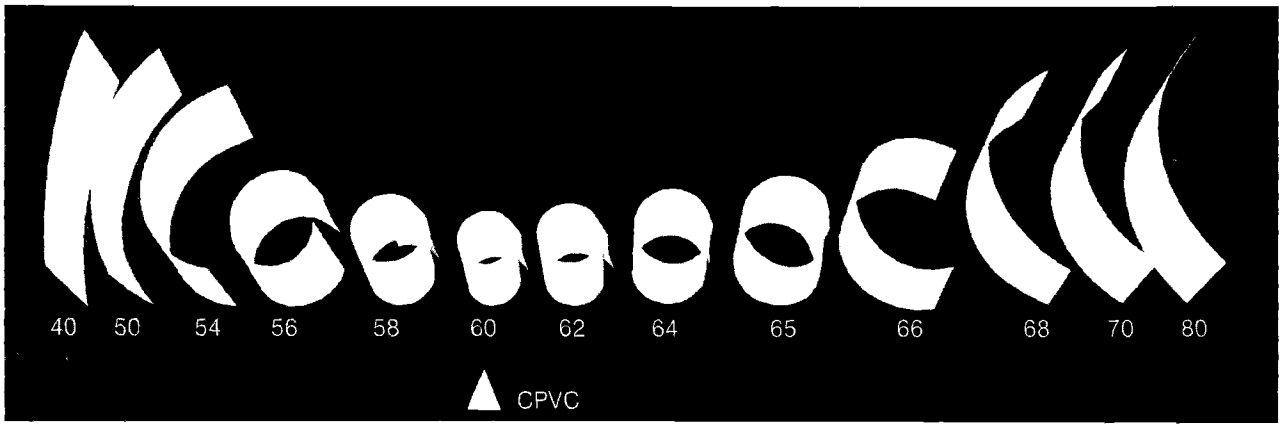

FIG. 18–Determination of the CPVC by comparing the curvature of painted plastic substrates [*57*].

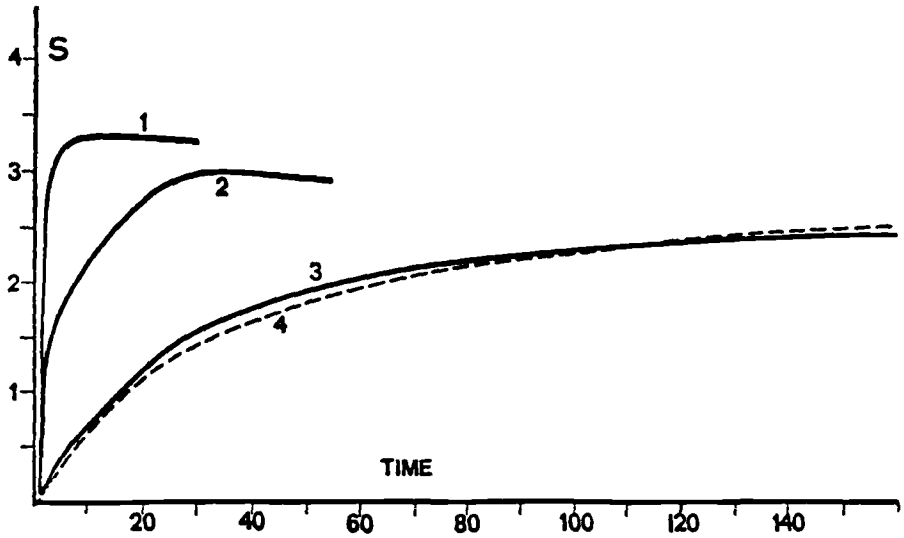

FIG. 19–Stress (*S*, MPa) as a function of time (day) in a thermoplastic varnish cast from methyl ethyl ketone and ethyl acetate (1); toluene (2); xylene (3); methyl isobutyl ketone and isobutyl acetate (4—), at 52% RH and 21°C [*16*].

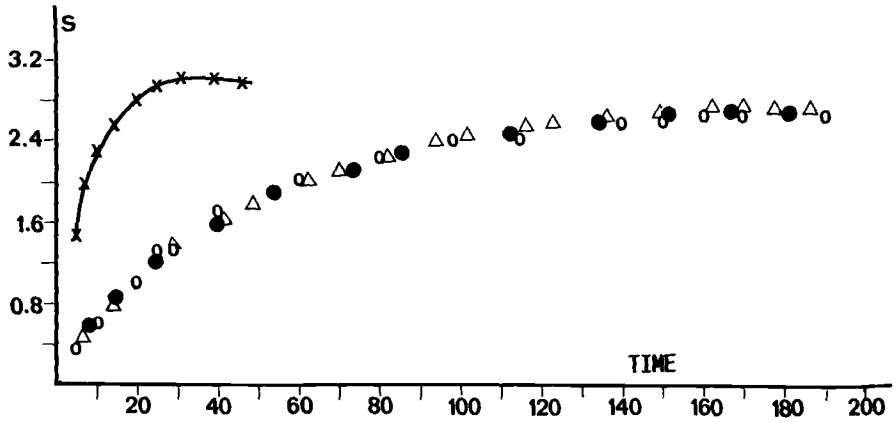

FIG. 20–Stress (*S*, MPa) as a function of time (day) for a thermoplastic varnish cast from toluene (X); isobutyl acetate (○), and their mixtures [1/1 (W/W) (●) and 1/3 (W/W) (△)] [*16*].

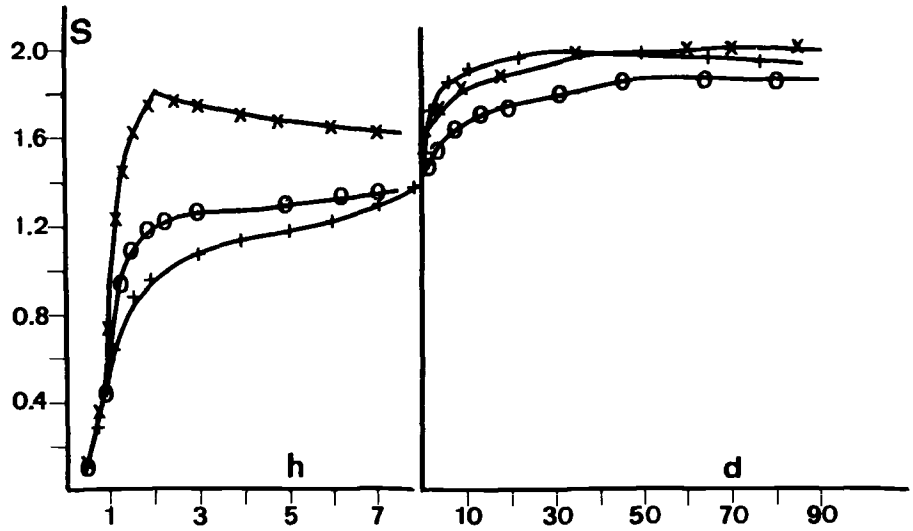

FIG. 21–Stress (*S*, MPa) as a function of time (h, hour; d, day) for a styrene acrylic latex paint containing different amounts of Texanol 5% (X); 10% (○); 15% (+): percent Texanol by weight of binder solids [*50*].

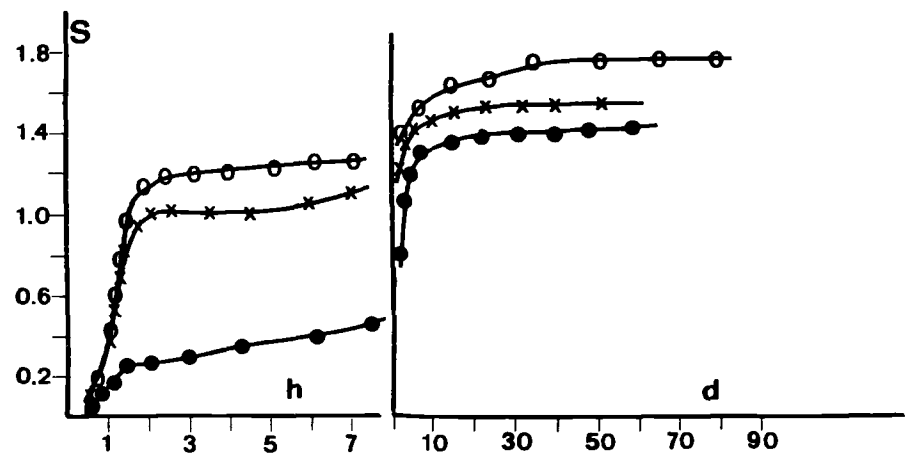

FIG. 22–Stress (*S*, MPa) as a function of time (h, hour; d, day) for a styrene acrylic latex paint containing Texanol (○); Dalpad A (X); Dalpad A + propylene glycol (●) [*50*].

Since stress develops in most organic coatings, the product $cS\epsilon$ should also be considered in adhesion tests performed in laboratories. The corrected mathematical equations for pull off and peeling at 90° are given by Eqs 21 and 22 [*61,67*], respectively

$$\sigma \approx \left[\frac{2K}{c}(\gamma - cS\epsilon)\right]^{1/2} \tag{21}$$

$$\frac{F}{b} \approx \gamma - cS\epsilon \tag{22}$$

where

σ = stress applied to pull the coating from the substrate,
K = bulk modulus of the coating,
γ = interfacial work of adhesion,
F = force applied to peel the coating, and
b = width of the coating.

Equations 20, 21, and 22 also indicate the possibility of determining the adhesion of a coating (i.e., the factor γ) without applying any external force. This is due to the fact that at a particular film thickness a spontaneous detachment should occur [*61*]. Unfortunately, this method can only be used for badly adherent coatings. For all other coatings, extremely high film thicknesses, difficult to apply and cure, would be necessary.

If the adhesion forces exceed the cohesive strength of a coating and the stress developed is high, damage will preferentially occur in the coating (cracking, fissuring) rather than at the coating/substrate interface. The verification of this principle can be realized by determining the stress and the ultimate properties of a coating. Since most of organic coatings are viscoelastic, it is essential that these properties be evaluated under the conditions (strain rate, temperature, RH) corresponding to the stress development in the coating. The presence of stress concentrations (e.g., existence of heterogeneities) in the coating and of a fatigue process are factors decreasing the overall stress at which the coating will crack.

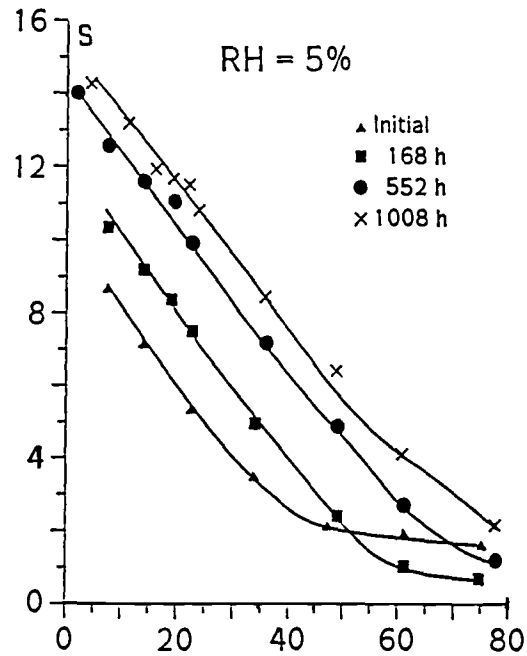

FIG. 23–Stress (*S*, MPa) as a function of temperature (*T*, °C) for a primer/clearcoat system after different periods of weathering [*9*].

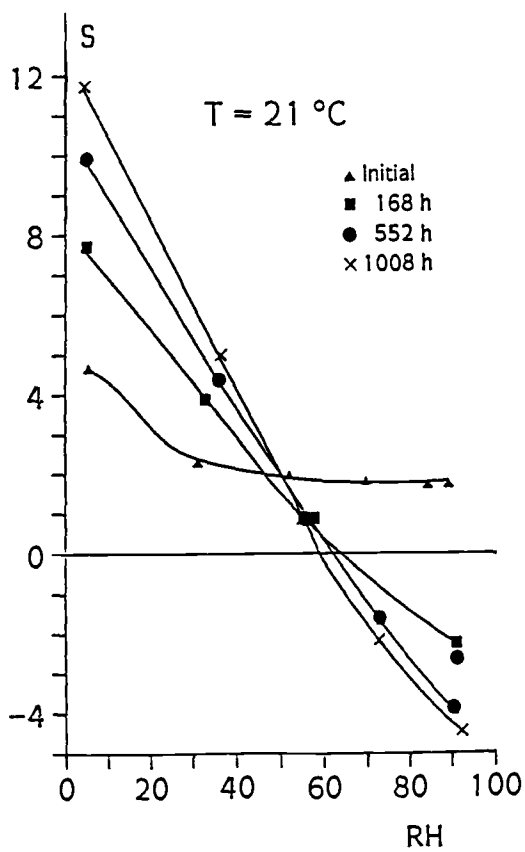

FIG. 24–Stress (*S*, MPa) as a function of RH (%) for a primer/clearcoat system after different periods of weathering [*9*].

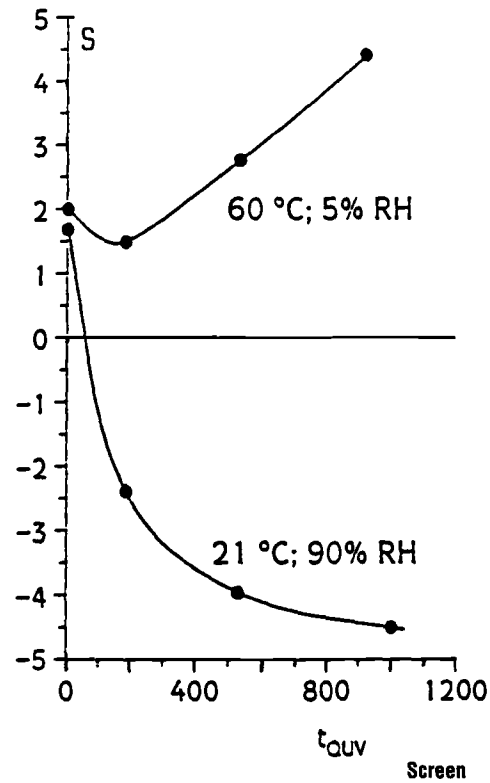

FIG. 25–Stress (*S*, MPa) as a function of time of weathering (t_{QUV}, hour) for a primer/clearcoat system at two climatic conditions [*9*].

WEATHERING AND STRESS DEVELOPMENT

In most cases when organic coatings are exposed to weathering (accelerated or natural), they undergo chemical and physical modifications which are expressed in the change of Tg, E, α, ν, and cross-link density. Under such circumstances and according to Eqs 1, 3, 5, and 10, one can also expect to see changes in stress development.

Confirmation of this and the role played by stress in the coating deterioration is given in Ref 9.

In this study a clearcoat/basecoat system exposed in a QUV apparatus to alternating dry and wet cycles cracked after about 1000 h.

By measuring the stress as a function of temperature and RH, it has been shown that weathering provoked: (1) an increase of Tg, which in turn induced higher tensile stresses (Fig. 23), and (2) an increase of coating sensitivity to moisture, which induced higher compressive stresses (Fig. 24).

The representation of the stress as a function of time of weathering for two experimental conditions similar to those present in the accelerating apparatus (Fig. 25) indicates that every time the experimental conditions changed (every 4 h) the coating was exposed to an increasing stress.

The processes thought to lead to fissuring of the clearcoat are described in Fig. 26.

Briefly, the chemical degradations induced by UV, water, and oxygen, which decrease the coating cohesion, combined

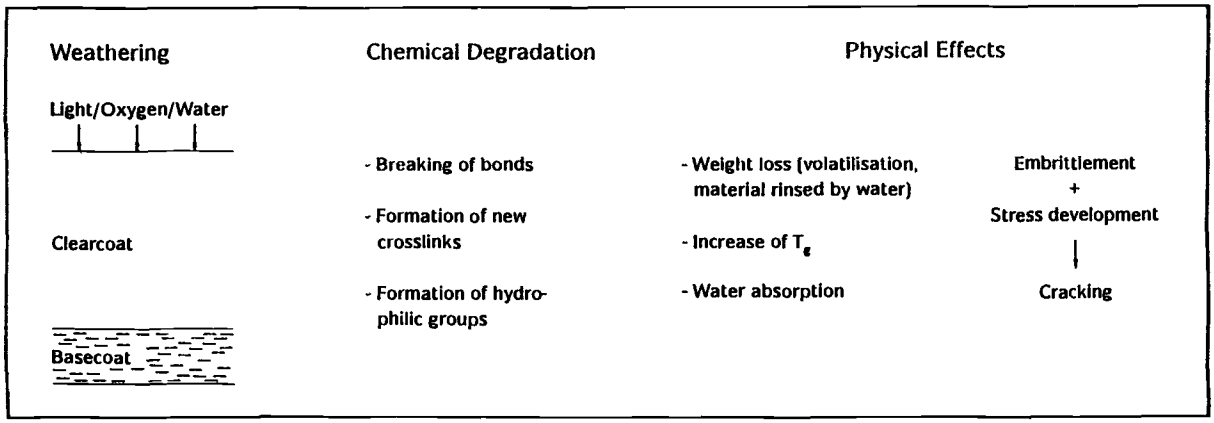

FIG. 26–Schematic representation of processes causing crack formation in a clearcoat [9].

with the fatigue process at steadily increasing hygrothermal stress levels are the causes of the coating degradation.

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Slip Resistance

by Paul R. Guévin, Jr.[1]

AN OVERVIEW OF THIS SUBJECT as it relates to the coating industry was published in 1978 [*1*]. This chapter is an expansion and update of that paper. Although a majority of the instruments and test methods for slip resistance were developed in ASTM committees with responsibilities other than for paint, they all can be used to measure the slip resistance of paints and coatings.

Specific standards for slip resistance and its testing mainly refer to flooring and other pedestrian walkway areas. At this time there are no coefficient of friction (COF) standards in the coating industry. One industry, the floor polish industry, established a COF value of less than 0.5 as a slippery surface and a value of greater than 0.5 as a not slippery surface [*2*]. OSHA has proposed that the COF for working surfaces, such as walkways and around machinery, in a plant be not less than 0.5 [*3*]. The U.S. Department of Justice has proposed a minimum COF of 0.6 for level walking surfaces and of 0.8 for ramps for its Americans with Disabilities Act [*4*]. If these proposals become law, painted walking surfaces must meet or exceed these standards.

ASTM ACTIVITY

Many studies of COF measurement by various ASTM committees occurred over the past 20 years. For the most part, these studies have been divided into specific committees with a task group of Committee F-13 on Safety and Traction for Footwear undertaking the task to improve communications between the various groups studying COF and thus prevent duplication of effort.

Task Group D01.23.15 on Slip Resistance is involved with measurement of paint and coatings COF. The group has developed a test method that describes a slip-angle test apparatus and a horizontal-pull slip meter that functions under wet and dry conditions and that can be used to measure both static and dynamic COF.

Other areas of activity dealing with the COF include ceramics [*5*], plastics [*6*], polishes [*7*], skid resistance [*8*], and footwear [*9*]. A study by the Consumers' Union [*10*] indicated a need for good measurement of slipperiness. Evidence in 1976 indicated that available instrumentation was inadequate and that results obtained with it did not correlate with practical observations. The National Institute of Occupational Safety and Health funded a project that dealt with slipperiness and safety of workers engaged in structural steel erection [*11*].

Definitions

The following are useful, specific definitions that have been developed by ASTM Committee D-21 on Polishes and found in ASTM Test Method for Static Coefficient of Friction of Polish-Coated Floor Surfaces as Measured by the James Machine (D 2047) [*12*].

Coefficient of Friction—The ratio of the horizontal component of force required to overcome friction, to the vertical component of the object weight or normal force applied through the object, which tends to cause the friction.

Dynamic Coefficient of Friction—The ratio of the horizontal component of force required to cause a body to slide at a relatively constant velocity to the vertical component of the weight of the object or force applied to it. The relatively constant velocity used to cause the body to slide over the surface is to be not less than 0.125 ft/s nor more than 0.5 ft/s (38 to 152 mm/s). The vertical component shall result in a contact pressure of not less than 1 psi (6.9 kPa) nor more than 13 psi (90 kPa) applied uniformly over the area in mutual contact.

Friction—The resistance developed between the physical contacting surface of two bodies when there is movement or tendency for movement of one body relative to another parallel to the plane of contact.

Slip Resistance—That property of a floor surface that is designed to prevent slipping. A surface having a static coefficient of friction of 0.5 or greater as measured in accordance with ASTM D 2047 is considered to be a slip-resistant surface.

Static Coefficient of Friction—The ratio of the horizontal component of force applied to a body that just overcomes the friction or resistance to slipping to the vertical component of the weight of the object or force applied to it. The vertical component shall result in a contact pressure of not less than 1 psi (6.9 kPa) nor more than 13 psi (90 kPa) applied uniformly over the area in mutual contact.

In a general sense, slipperiness can be defined as the tendency or liability to cause something to slide suddenly or involuntarily. In many cases, an organic polymer surface (i.e., a coating) is involved. In terms of the flooring market area, for which these definitions were written, the flooring surface

[1]Consultant, P. R. Guévin Associates, P.O. Box 811, Westerville, OH 43086-0811.

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could be an alkyd enamel on a porch or deck, a vinyl- or polyurethane-coated athletic gymnasium floor, a waxed vinyl-composition floor tile, an epoxy-coated concrete factor floor, and so on. Slipperiness can be considered as being made up of two factors, skid resistance and slip resistance. Skid can be defined as an act of sliding without rotation and slip as a slide that occurs suddenly or involuntarily.

CONCEPT OF THE COEFFICIENT OF FRICTION

Slip is a word that has many meanings [*13,14*]. In certain areas of the coating industry, slip is considered to be the ability of an object to move in a relatively free or unencumbered but controlled manner when one sheet of metal passes over another sheet as in a coating-line feeding operation, when it moves along a conveyor system in coating, printing, fabrication, or packaging operations, and the like. The coating must have proper "slip" or "lubricity" to allow the coated object to pass through the coating system to a further fabrication or packaging section of the line. In fact, slip is very important to fabrication operations wherein the coated object is in contact with a tooling system as in fabrication of bottle caps, or with other metal surfaces in bending operations, etc. Yet, other coatings such as floor coatings are designed to decrease this ability to move easily under an applied force. In either case, the frictional resistance between objects is being modified and controlled with such control being attained by the inherent properties of the materials used for the coating or use of additives in the coating. It is important to understand that at times low friction is desired and that at other times reasonably high friction is desired.

Friction is the property that determines the degree of slip or resistance to slip that exists. Both static and dynamic or kinetic friction are important properties of coatings. Static friction is the amount of friction between two surfaces at the precise instant when one commences to move over the other. Dynamic friction is the friction between two surfaces when they are moving past one another without interruption. The coefficient of static friction is usually equal to or greater than that of dynamic friction [*15*]. The coefficient of friction, μ, is a measure of slip with a high coefficient of friction denoting poor slip and a low coefficient of friction denoting good slip [*16*]. This parameter is the ratio of the force F (frictional force) required to move one surface over another surface to the total force W pressing the two surfaces together

$$\mu = F/W$$

A current theory of the mechanism of dry friction describes the force of friction arising from the shear strength of minute interaction areas or areas of true contact between the contacting surfaces. These interaction areas are distributed in a more or less random manner over the total apparent contact area. This can be expressed by the following relation for the friction force

$$F = s \cdot A$$

where s is the average shear strength of the interaction areas, and A is area of actual contact. Since it is the interaction areas that actually carry the normal load W between the two surfaces, the following relation also exists

$$W = \rho_m \cdot A$$

where ρ_m is defined as the flow pressure of the softer material in the vicinity of these local areas of true contact. When A is eliminated between these equations, the friction coefficient is obtained

$$\mu = F/W = s/\rho_m$$

Friction is the universal force between surfaces that opposes sliding motion. When surfaces of bodies are in contact, the interactive force at the surface may have components both perpendicular and tangential to the surface. The perpendicular component is called the "normal force," and the tangential force is called the "friction force." When there is relative sliding between the bodies, the frictional force always acts in the opposite direction of this motion.

Most dry surfaces behave approximately and within limits according to Coulomb's frictional law. Coulomb found that just before motion, the friction between two surfaces is slightly greater than when the surfaces are in steady motion relative to each other, that the frictional force is proportional to the normal force pressing the surfaces together, and that this force is independent of both the contact area and, except at the start, the speed of relative motion of the bodies. The constant ratio of the tangential force to the normal force is known as the "coefficient of friction" (COF) and depends on the nature of the two surfaces. To initiate sliding against friction, it is necessary to apply a tangential force at least as great as the COF and the normal force before the onset of motion take place. The applied tangential force is resisted by the equal and opposite force of static friction, and the force required to overcome static friction is usually greater than the force needed to sustain uniform sliding motion.

DETERMINATION OF THE COEFFICIENT OF FRICTION

Three types of instruments are used to measure the COF, and these are illustrated in Fig. 1 [*17*]. These are drag-type meters that are based on $\mu = F/W$, pendulum-type meters that measure the energy loss of the pendulum as an indirect indication of the dynamic friction, and articulated-strut devices that are based on the direct and fundamental principle of the resolution of forces that take place when an object slides down an incline as described below. The angle at which a flat or plane surface must be inclined for a solid object to slide with a steady speed down the incline is the "angle of friction." The tangent of this angle is the COF between the solid block of material and the inclined plane

$$\mu = \tan\phi$$

The principle involved in this equation is used in the slip-angle apparatus described in ASTM Test Methods for Measuring Static Friction of Coatings Surfaces (D 4518) [*18*]. The state of the art of slip-resistance studies through 1975 has been summarized by Brungraber [*19*].

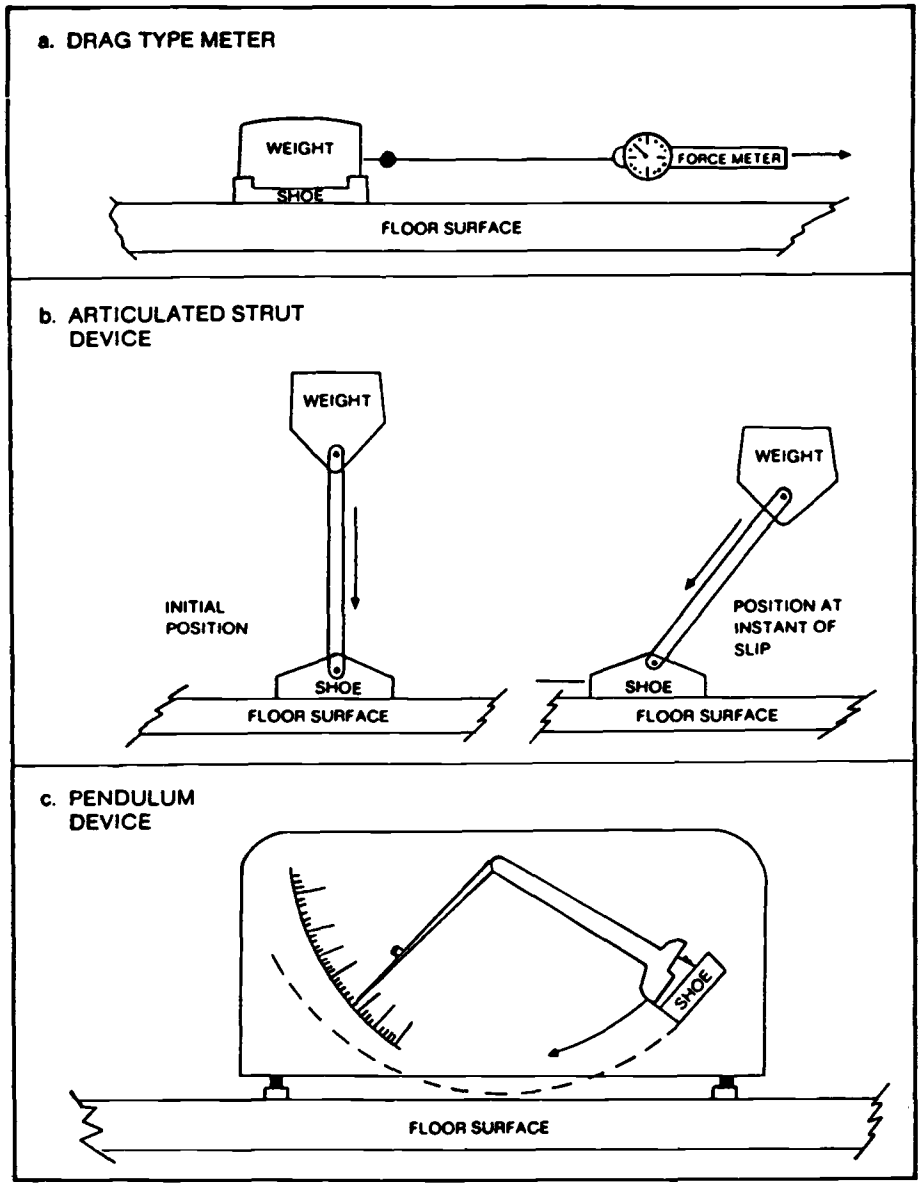

FIG. 1–Schematics of different friction measurement devices (courtesy of the National Institute of Standards and Technology).

SENSOR MATERIALS

It is obvious that two surfaces are required for COF measurements of any surface, and the sensor material, or surface against which the specified compound is tested, should be defined and specified. It is essential to obtaining meaningful, reproducible results that the sensor material be selected to represent use conditions and be well defined. Properties such as uniformity (surface character including flatness, roughness, chemical composition, resilience, and shear modulus), permanence in that chemical and physical characteristics should not change with time, and availability in a usable form that does not require excessive preparation should all be considered when selecting a sensor. Both sensor material and test material should be reported when the coefficient of friction is given.

The sensor material may be composed of the same compound as the test compound or different. In most ASTM studies of flooring, leather is used as the primary sensor material. It is commonly used in the manufacture of shoes, and, probably more important, it has the lowest COF of any shoe-sole material. Although the rationale for its selection is not well documented, leather conforming to Federal Specification KK-L-165C is specified as the sensor material. Where a nonleather sensor material is to be used, rubber conforming to ASTM Test Method for Rubber Property—Abrasion Resistance (NBS Abrader) (D 1630) [*20*] is used. Neoprene has been used in certain round-robin studies. In other instances, three leathers with three levels of oil content, two Kraton® thermoplastic elastomers, and 15 different rubbers were used to generate statistical data [*21*] for ASTM Test Method for

Static Slip Resistance of Footwear Sole, Heel, or Related Materials by Horizontal Pull Slipmeter (HPS) (F 609) [22].

LUBRICANTS

In those instances where slip is to be increased (friction decreased), a variety of slip agents or lubricants are available. These include micronized polyethylene powders and silicones. See Table 1 for more slip agents. Many slip agents also function as abrasion-resistance and mar-reduction agents. In certain instances, they can be used as antiblock agents. Lubricants are often used in the plastics processing industry where they function as melt viscosity reducers, flow agents to improve flow onto metal surfaces, and, at times, costabilizers. Factors that should be considered in selecting a lubricant include melting point, polarity, and solubility. Of course, the lubricant should not interfere with adhesion or any cross-linking mechanism that is used. Common lubricant families as well as selected specific lubricants are listed in Table 1. Polyethylene and polytetrafluoroethylene are available in a powder or micronized form in a variety of particle sizes [23], and silicones are available as formulated products designed for use in the coating industry [24,25]. The micronized polymers are incompatible and act as a filler that rises to the coating surface where they function as tiny "ball bearings" that decrease friction and often improve abrasion and mar resistance.

TABLE 1—Lubricants.

Esters
Wax esters
Fatty alcohol esters
Fatty esters
Glycerol esters
Fatty Acid Amides
Alkanolamides
Monoamides
Bisamides
Metallic Compounds
Aluminum stearate
Barium stearate
Calcium stearate
Molybdenum sulfide
Zinc stearate
Waxes and Other Hydrocarbons
Fluoropolymers
Micronized polyethylene
Micronized polytetrafluoroethylene
Montan waxes
Oxidized polyethylene waxes
Paraffins, low melting
Polyethylene waxes
Silicones

METHODS FOR DETERMINING COEFFICIENT OF FRICTION

The test methods and equipment described below were developed for flooring materials. However, they can be applied to testing the slip resistance and COF of paint and coatings on various substrates against themselves as well as against a variety of substrates.

ASTM Test Method for Determining the Static Coefficient of Friction of Ceramic Tile and Other Like Surfaces by the Horizontal Dynamometer Pull-Meter Method (C 1028-84) [26] utilizes a pull meter-and-heel assembly to measure the COF of tile and like materials. The test method specifies a standard ceramic tile with an average COF between 0.45 and 0.55 and a neolite sensor material. Currently consideration is being given in an ASTM subcommittee to modifying this device for improved reproducibility or discontinuing the method.

ASTM Test Method for Static and Kinetic Coefficients of Friction of Plastic Film and Sheeting (D 1894) [27] is concerned with determination of static and dynamic COFs. The test method specifies only the force-measuring instrument since the test method uses a plastic film or sheet sliding over itself. One company that manufactures slip-resistance coatings intended for compliance with OSHA and ADA requirements specifies this test method for determination of product COF.

ASTM Test Method for Static Coefficient of Friction of Polish-Coated Floor Surfaces as Measured by the James Machine (D 2047) [12] is the only slip-resistance test method recognized by the floor-polish industry. Unfortunately, its use is limited to the laboratory since it is not portable. Sensor materials of leather and rubber are specified.

Method A of ASTM Test Methods for Measuring Static Friction of Coating Surfaces (D 4518) [18] involves a platform containing a sled that is slowly raised until the angle of movement is reached. Method B involves a horizontal-pull tester. Some laboratories have modified their Instron tensile testers to perform similar operations. This approach has the advantage of providing a graphic record of the forces involved.

Other ASTM methods for measuring friction include ASTM Test Method of Measuring Surface Frictional Properties Using the British Pendulum Tester (E 303) [28], ASTM Consumer Safety Specification for Slip-Resistant Bathing Facili-

TABLE 2—Canadian government standards for coefficient of friction.

	Static COF			Sliding COF		
	Dry	Wet	Oily	Dry	Wet	Oily
For leather with:						
Epoxy coating	0.75	0.75	···	0.50	0.50	···
Polyurethane coating	0.85	0.85	···	0.50	0.50	···
For rubber with:						
Epoxy coating	1.00	0.90	0.70	0.80	0.80	0.40
Polyurethane coating	1.00	0.85	1.00	0.85	0.85	0.70

TABLE 3—Devices for measuring the coefficient of friction.

Device	Manufacturer	Comment	Reference
		DRAG-TYPE FRICTION MEASURING DEVICES	
Dynamometer Pull Meter	Chatillion Inc.	Tests are being discontinued by ASTM C21.06	
Gardco Washability Wear Friction Tester, Model D 12VF	Paul N. Gardner Co. Inc.	Instrument is being evaluated at several companies	[*27*]
Coefficient of Friction Tester, Model FM-1055 and -1055F	Paul N. Gardner Co. Inc.	Meets ASTM D-1894-78 requirements. Model F has a force transducer for strip chart readout.	[*27*]
Instrumentors Slip/Peel Tester Model SP-101B	Instrumentors, Inc., Cleveland, OH; available from IMASS, Accord, MA	Designed to meet ASTM D 1894	
Floor Friction Tester, Model 80	Technical Products Co.	Portable device	
TMI Slip & Friction Tester, Models 32-06	Test Machine Inc., Amity, NY	Flat bed plate laboratory horizontal pull slipmeter	
TOPAKA® Horizontal Slip Tester	Pioneer Eclipse Co.	Described in ASTM D-21 Proposal P 128	[*7*]
Universal Slip-Resistance Tester	William English Ltd.	Device has been removed from market	[*29–32*]
Whiteley Model HPS III Slip Master	Whiteley Industries, Inc.	Can be used to test in accordance with ASTM F 609	
		DYNAMIC PENDULUM-TYPE SKID RESISTANCE TESTER	
British Portable Skid Resistance Tester	Road Research Laboratory, Crowthorne, Berkshire, England	ASTM E 303 utilizes this device	[*28*]
Sigler Coefficient of Friction Machine	Frazier Precision Instrument Co., Hagerstown, MD	Specified in Federal Test Method Standard No. 501a	[*33–34*]
Tortus Floor Friction Tester	Ceramic Research, Penkhall Stake-on-Trout, England	Very good for microinvestigations of floor surfaces	[*35–38*]
		ARTICULATED STRUT TESTERS	
Ergodyne Slip-Resistance Tester	William English Ltd., Alva, FL	Small and lightweight in nature	
James Machine	AIDE, Inc., Racine, WI	Used in ASTM D 2047. Considered to be a comparison standard testing device.	[*12,39*]
NBS/Brungraber Slip Tester, Model Mark I and Model Mark II	Slip-Test Inc., Lewisburg, PA	Mark I useful on dry surfaces and Mark II useful on wet surfaces	[*5,32,40–41*]
Model 9505 Mobility/Lubricity Tester	Altek Co., Torrington, CT	Used to measure slip resistance such as beverage exterior can coatings	

ties (F 462) [*22*], ASTM Test Method for Static Coefficient of Friction of Shoe Sole and Heel Materials as Measured by the James Machine (F 489) [*22*], and ASTM Test Method for Static Slip Resistance of Footwear, Sole, Heel, or Related Materials by Horizontal Pull Slipmeter (HPS) (F 609) [*22*].

Few slip-resistance standards exist in most industries, including the coating industry, even though there are many painted surfaces in pedestrian walkways. The United States Navy has two specifications—MIL-D-23003A Military Specification-Deck Covering Compound, Nonslip, Rollable and

MIL-D-24483A Military Specification-Deck Covering, Spray-On, Nonslip—that specify COF values. Both specifications use horizontal slip testers.

The Canadian Government Specification Board adopted two standards for deck coatings based on the above U.S. Navy specifications. One involves nonslip epoxy coatings, 1-GP-192, and the other nonslip involves polyurethane coatings, 1-GP-200. The COF specifications for these materials are given in Table 2. This information points out some important aspects of slip resistance measurements. First, value differences in slipperiness of various shoe-sole materials under different conditions are used. Second, it points out the importance of specifying the nature of the shoe-sole material. Overall, leather has lower COFs than rubber.

TEST DEVICES FOR MEASURING THE COF

As mentioned earlier, there are three types of devices used to measure the COF, namely drag, pendulum, and articulated strut-based devices. The drag-type meters can be subdivided into two classes: (1) horizontal-pull slip meters that are portable, inexpensive, and used directly on a floor or other surface under test and (2) bench-top slip meters that are used primarily in the laboratory. Both of the devices in these subclasses are sometimes referred to as "fish scale-type testers." The devices are simple, motorized power units with force-measuring devices such as dynamometers. One such device, developed at an insurance company [*42*], has been used by an ASTM subcommittee in a round-robin study [*21*] to evaluate walkway slipperiness [*43*]. Use of such devices has been validated in another study [*44*]. General results from some ASTM members indicates that pendulum-type devices are not applicable for further consideration in the measurement of the COF.

Pendulum-type COF devices [*12,33–34*] consist of a pendulum that is faced with a certain shoe-sole or heel material. The pendulum can be adjusted to sweep a path across a flooring surface so that the contact pressure between the facing and the floor follows a predetermined, time-dependent pattern. The pendulum's resultant loss of energy is purported to be a measure of the dynamic friction.

Articulated-strut meters [*12,39–41*] involve application of a known, constant vertical force to a shoe that is faced with a particular sole or heel material along with application of an increasing lateral (forward) force until slip occurs. The ratio of the lateral force at slip to the known vertical force is the static COF. The vertical force is applied to the top so that the article tested is only subjected to a vertical load. As the test progresses, the articulated strut is slowly inclined so the test article continues to be under a constant vertical load and in addition under an increasing horizontal or tangential load until slip occurs. The tangent of the angle that the articulated strut makes with respect to the vertical at the instant of slip is taken to be the ratio of the horizontal and vertical components of the force applied to the show and thus is the COF.

Devices of the three types are summarized in Table 3.

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Part 12: Environmental Resistance

51

Prevention of Metal Corrosion with Protective Overlayers

by William H. Smyrl[1]

THE PREVENTION OF CORROSION BY SURFACE PROCESSING enjoys significant economic leverage, and, as evidence, one may cite the widespread use of coatings, films, and inhibitors for metals and semiconductors in many service environments. All engineering metals used in modern technological societies are unstable with respect to corrosion, and the result is a loss of properties. Natural oxide films provide protection against continued attack for some metals, and alloying extends the life of other metals by developing highly stable passive films. Where metals may not be protected by oxide films, other modification methods have been developed to reduce corrosive attack. In reality, the improvement of corrosion resistance of metals by modification of the surface has been practiced since the invention of metal tools. Some of the earliest techniques to prevent corrosion involved coating with greases or natural oils. More modern methods were developed in the 19th and 20th centuries and include multiple coatings, zinc galvanizing, electroplating of other pure metals, and vacuum physical vapor deposition of mostly pure metal coatings by electron beam and sputtering techniques. The metal coatings are better barriers than organic films because of the lower permeability of the former to moisture, oxygen, and ions. Inhibitors or conversion coatings and primers for paints are cheaper than metal coatings and are used widely by paint manufacturers even though they remain highly proprietary in nature.

The use of organic coatings to protect metal surfaces is practiced widely. Much of the use is for atmospheric exposure of motor vehicles as well as for structural units such as bridges and buildings. The successful implementation of existing technologies has greatly reduced the effects of corrosion of automobiles, for example, in the past decade in response to consumer demand. Despite many recent advances, coating technologists and scientists acknowledge that much is unknown and that new processes and understanding are the keys for further progress [*1*]. Defects in the metal substrate and in the overlayers are among the primary concerns because they are the source of localized corrosion phenomena. Defects may occur on length scales from atomic-level lattice vacancies to arrays of defects at grain boundaries (for crystalline materials) or to random pores or cracks (for example, in noncrystalline films). Avoiding such defects by proper quality control is a major concern in coatings science and technology.

[1]Professor, Corrosion Research Center, Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455.

In the discussion that follows, aspects of corrosion that involve thermodynamics and kinetics will be developed as a basis for the description of the specific nature of corrosion of metals under protective films and overlayers. Some emphasis will be given to protection of thin metal films and microstructures that are particularly sensitive to corrosion and whose successful protection provides a basis for advancing protection technology in general.

CORROSION IN AQUEOUS SOLUTIONS

The driving force for a reaction is the change in Gibbs free energy, ΔG, for reactants to products. Mathematically, this may be expressed by

$$\Delta G = \sum_{\text{products}} G - \sum_{\text{reactants}} G$$

The summation signs are used as a general notation to indicate that all reactants and products are included in the calculation. From the nature of the free energy function, this calculation applies to initial (reactants) and final (product) states and is independent of intervening states. The reaction may be investigated under controlled reversible conditions such as in an electrochemical cell or under irreversible conditions such as in corrosion, and the same total free energy change (ΔG) will be appropriate. A quite general predictive capability may be applied to specific corrosion reactions since all the available thermodynamic data may be used for corrosion calculations directly. This enables the position of final equilibrium of the corrosion system to be established. The thermodynamic calculations have the limitation that no information concerning the *rate* of the reaction is provided, only what the final state will be for the process.

The value of ΔG for reactions of elements to form a compound, all in their standard states at a particular temperature, is the standard free energy of formation of the compound, $\Delta G^0_{f,T}$. Here, the subscript T denotes the temperature. Description of the detailed calculations are beyond the scope of this discussion, but several excellent textbooks are available [*2,3*].

The most extensive tabulations of thermochemical data for chemical compounds in their standard state at 25°C are in a series of National Bureau of Standards publications [*4*]. These are NBS Technical Notes 270-3, 270-4, and 270-5, which supersede the older NBS Circular 500 for the elements they cover. These tabulations also update the older data of

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Latimer [5]. The book by Latimer [5] remains a valuable reference because of the description of techniques to estimate thermodynamic quantities where reliable data are sparse. Lewis and Randall [3] tabulated thermodynamic data, including data for aqueous solutions of a number of electrolytic solutions that are valuable for corrosion calculations. There is overlap between this tabulation and the JANAF thermochemical tables [6], but the latter also tabulate the standard enthalpy and free energy of formation of chemical compounds at several temperatures along with $-(G^0 - H^0_{298})/T$.

Oxide and hydroxide solubility are strongly influenced by the pH of the aqueous phase. Pourbaix recognized this and summarized the thermodynamic stability of metal-aqueous systems by the use of potential-pH diagrams. The thermodynamic data tabulations already quoted [3–6] should be utilized for detailed calculations, however.

Usually when studying corrosion, one is not concerned with the conditions for thermodynamic stability, but rather with the rate of attack and how it may be altered in basically unstable conditions because only a limited number of systems have absolute or *thermodynamic stability*. As a practical matter it is necessary to accept some rate of corrosion and/or to control or mitigate the rate of attack. Thus *kinetic stability* is always relative and subject to interruption if control is not maintained. Controlling the rate of degradation may be accomplished, for example, by the use of cathodic or anodic protection, the use of inhibitors, the maintenance of protective surface films, or buffering the composition of an otherwise aggressive solution. All these techniques are used widely to extend the life of metallic structures with continuing improvement.

Corrosion reactions are electrochemical in nature. The kinetics of the corrosion reactions are then related to the kinetics of the electrochemical reactions that occur during the corrosion process. The reactions involve not one but at least two electron transfer reactions, and the reactions are not in series but are in parallel. Coupling of parallel or simultaneous reactions is a fundamental feature of the corrosion process. Each of the simultaneous reactions may consist of multiple steps, respectively, as described above, but the simultaneous, independent reactions are coupled electrically. The independent reactions occur on the same surface at the same time, but also at the same potential. The reactions may be coupled chemically as well, e.g., through pH effects, but this is not essential. The specific relation that defines the coupling of simultaneous corrosion reactions on an isolated metal surface is

$$\sum_{\text{anodic}} I_a = -\sum_{\text{cathodic}} I_c$$

There will then be zero net current to the corroding metal electrode. The relationship is written in terms of currents (I_a and I_c) rather than current densities for reasons which will be discussed. The potential at which the balance is satisfied is the mixed or corrosion potential. It is determined by the rates of the simultaneous reactions and is not defined by the state of the system in a thermodynamic sense. The corrosion potential always lies between the equilibrium potentials of the anodic and cathodic processes, respectively.

As a summary, the general corrosion of metallic materials in aqueous solutions is well understood. The anodic or oxidation reaction of the metal is superimposed on a cathodic reaction, and the two are balanced locally on a homogeneous surface. The rate of the reaction is a function of both the rate of metal dissolution and the rate of the cathodic (reduction) reaction. Each reaction may be influenced in general by the composition of the solution, especially the pH and the electrolyte anion, and by the nature of the (oxide) films, if any, which may be formed at the metal/electrolyte interface. If several oxidizing species are present in the solution, each may act in parallel so that the total rate of metal dissolution is increased. For example, most metals will react directly to displace hydrogen from water and to produce an oxide of the metal or some other corrosion process. The addition of oxygen will increase the rate of corrosion of the metal, usually in direct proportion to the concentration of the oxygen added. The specific details will vary with each metal to reflect the thermodynamic, kinetic, and mass transfer driving forces that are acting [7].

Heterogeneous surfaces are commonly observed in corrosion situations and are of the three general classes: (1) the inclusion of foreign metal impurities on the metal surface, (2) the nonuniform coverage of the surface by a film, either an oxide film or an artificial coating in aqueous solutions, and (3) nonuniform conditions in the electrolyte environment. All these are of great importance because localized, or nonuniform, corrosion of metals may be caused by any of the three. A form of galvanic corrosion and pitting corrosion is caused by the first type of heterogeneity, while crevice and pitting corrosion are produced by both (2) and (3).

Restrictions of geometry, e.g., in crevices and corners, prevent mixing of solutions everywhere, and local buildup of reaction products or the exhaustion of an oxidant may occur. The local kinetics will be relatively independent of that in other regions except that there may be coupling through the electric field and electrical current may flow between a localized corrosion site and the surrounding surface. This may lead to nonuniform corrosion, particularly where the buildup of products increases the aggressiveness of the local solution. In this case, corrosion will be most severe, not where the concentration or flux of the bulk solution oxidant is highest but where it is lowest. Crevice corrosion is considered to be an example of this type of attack, and the aggressive solution within a crevice or pit is one which is more acidic than the external solution.

Anodic dissolution, plus hydrolysis of the product metal ion, causes an increase of hydrogen ion concentration. On the other hand, reduction of either hydrogen ions or dissolved oxygen reduces the hydrogen ion concentration. If the net corrosion reaction plus hydrolysis would lead to an increase of hydrogen ion concentration, the process may occur independently of any other process and would accelerate with time to some steady state where diffusion out of the occluded region would limit the buildup. If the corrosion reaction plus hydrolysis leads to no net change in H^+ concentration, an acid solution in a crevice or pit could only be created by separation of the anodic and cathodic regions. Concentrating the cathodic reaction on the outer surface would occur naturally if dissolved oxygen, for example, were the primary bulk oxidant. Coupling this with a net anodic reaction (plus hy-

drolysis) in the inner region for an overall current balance would lead to a steady state crevice or pit.

For separation to occur as described above, a quite general condition imposed on the corrosion kinetics must be obeyed. The outside surface must support a cathodic reaction, and it must be supported at a potential that is positive of the potential of the anodic reaction in the crevice. The direction of current flow through the solution establishes this criterion. A qualitative laboratory test may be used to identify metal solution combinations that could cause localized attack by the mechanism described above. The test involves the corrosion kinetics on the metal of interest. Cathodic currents must be observed on the metal in the exterior solution at potentials that are positive of the anodic region for the crevice conditions or the separated reactions will not support increased anodic dissolution in the isolated region. This is a very definitive test, and very few metal-environment combinations match the criterion.

Ohmic drop restricts the penetration of current into a small-gap, occluded region [*8*]. This causes the anodic reaction to be distributed over a relatively small region, which concentrates the attack. At greater depths in the gap, the metal is isolated from the external surface reactions. Newman [*9*] calculated the limited depth to which a reaction may penetrate inside a circular geometry, in this case a cathodic protection reaction. The reaction is concentrated near the opening.

Composition gradients are considered to be important for pitting and differential aeration corrosion as well. For pitting corrosion, similar conditions to those for crevice corrosion are considered important. Pits may be initiated in ways that are different from crevice corrosion, e.g., at foreign metal inclusions. However, the propagation of pits depends largely on a locally aggressive solution. Stirring to eliminate concentration effects will stop the growth of pits. Differential aeration could also drive corrosion at locally variable rates under an electrolyte film of nonuniform thickness. The diffusion-limited flux of oxygen through the film would be directly proportional to the film thickness. If the local corrosion rate is limited by the oxygen flux, the attack will be most severe at low film thicknesses. For active/passive metals, increase of the oxygen flux may exceed the peak current for active dissolution and cause the metal to adopt the passive state. In this case, then, thin films of electrolyte will *reduce* the corrosion rate.

ATMOSPHERIC CORROSION OF METALS

Most atmospheric corrosion tests have been conducted in environments such as indoor atmosphere, outdoor atmosphere, and laboratory tests under simulated conditions. Indoor corrosion studies have been performed for the electronics, computer, and communication industries for the development of more durable materials with desirable structural, magnetic, and electrical properties. On the other hand, outdoor studies aimed at understanding corrosion behavior are highly dependent on atmospheric weather factors, especially in marine and urban areas. The latter studies have been performed in the automobile, marine, and aircraft industries. Laboratory tests attempt to use accelerated methods under simulated atmosphere or aqueous conditions. Electrochemical methods have been used extensively in such tests to analyze and monitor the corrosion behavior of metals.

Several weather factors are known to influence outdoor corrosion [*10–13*]. Precipitation, ambient and dew-point temperatures, atmospheric pollutants, wind direction and wind velocity, and solar radiation can be considered as weather factors in outdoor and/or urban corrosion tests. Among these factors, moisture or relative humidity, temperature, and pollutants such as sulfur dioxide and chlorides are the most important variables.

Relative humidity is known to be the most important factor in determining the atmospheric corrosion rate. It has been reported that rapid acceleration of corrosion occurs beyond a certain value of relative humidity, defined as the critical humidity [*14–15*]. The period in which the relative humidity exceeds the critical humidity is called the time-of-wetness, and this factor is quite significant in determining atmospheric corrosion rate of metals [*16*]. In addition, in the presence of a pollutant such as sulfur dioxide, the critical humidity at which corrosion is enhanced to a significant extent will decrease with increasing pollutant concentration [*17–18*].

It has been reported that comparatively large aggregates of water are present on oxyhydroxide surfaces at humidities below 40% [*19*]. Even on clean metal surfaces obtained under ultrahigh vacuum or reducing conditions, significant quantities of water are adsorbed on air-formed films when exposed to the environments containing only oxygen and water vapor for more than a microsecond [*13*]. As a result, monolayers of adsorbed water may provide the medium for electrochemical microcells that may drive a heterogeneous corrosion process. Water may also exist in the form of complex mixtures with oxides, hydroxides, and mixed oxyhydroxides [*19–20*].

The corrosion rate of metals is accelerated by the presence of air pollutants such as sulfur dioxide, nitrite, nitrate, hydrogen sulfide, chloride, and some kinds of salts [*10,15*]. These species may derive from gas-borne particles or from reactions at the surface. Reaction with adsorbed water monolayers yield electrolyte films that facilitate further corrosion processes. Among these pollutants, sulfur dioxide, chlorine gases, sulfur gases, and ozone are important species that promote corrosion in the presence of water.

The corrosion-accelerating effect of sulfur dioxide with humidity has been reported by many investigators [*10,13,15*]. Vernon [*15*] suggested that sulfur dioxide may change the pH in electrolyte films present on metal surfaces and enhance the corrosion rate. Rice et al. [*13*] also suggested that sulfur dioxide is readily soluble in water to form sulfurous acid; these local acidic regions accelerate oxide formation, and the corrosion rate is also enhanced by other electrochemical effects. It has been reported that wetting of the metal surface is promoted in the presence of ammonia, and the water droplets contain higher concentrations of sulfates than for the same concentration of sulfur dioxide with no ammonia [*10,22*].

The effect of chlorine gas or chloride on atmospheric corrosion has been reported [*10,13*]. In aqueous electrochemical corrosion studies, the chloride ions usually enhance pitting corrosion of many metals and also degrade the oxide surfaces. Rice et al. [*13*] reported that chlorine gases reduce the surface pH and yield hygroscopic corrosion products that influence the amount of adsorbed water. A direct relationship

between the amount of chlorides in corrosion products and atmospheric corrosion rates was reported by Sereda [*10*].

The effect of ozone gas on copper and silver corrosion has been known to be significant, while cobalt, nickel, and iron are insensitive to ozone [*13*]. It has been reported that ozone may enhance the corrosion rate of metals sensitive to H_2S.

The atmospheric corrosion rate can be measured either in field tests in different atmospheres or with accelerated tests in the laboratory. The field tests require long exposure times and yield complicated data that prevent detailed analysis. Accelerated tests are performed under simulated atmospheric conditions, and they are the easiest way to acquire more information with various setup conditions. However, it may not be possible to simulate practical service conditions.

There are several methods to monitor and control the corrosion rates by means of either field or laboratory tests. The conventional method is the weight loss determination, which requires long-term exposure unless a continuous method is used that involves the quartz crystal microbalance [*23–24*]. Another method is the electrical resistance method and measurement using electrochemical cells. Electrical resistance methods use the changes in the electric resistance of thin wires or foils to monitor failure, but they cannot be used for determination of the instantaneous corrosion behavior [*25–27*].

Electrochemical methods have been developed to take advantage of the electrochemical basis for atmospheric corrosion [*28–29*]. Corrosion currents can be monitored electrochemically, and the instantaneous value of current can be detected. One way to monitor atmospheric corrosion with an electrochemical method is to design a cell that will work under thin electrolyte layers (less than 500 μm) with consideration of the effects of corrosion products and dilute pollutants [*30*].

Electrochemical methods for monitoring atmospheric corrosion have been well reviewed by Mansfeld [*30–31*]. Most of the studies have been aimed at macroscopic measurement of time-of-wetness that is associated with electrochemical corrosion [*10,12,16,17*]. Galvanic cells with electrodes of different metals have been commonly used [*16,32*]. Sereda [*10*] has developed galvanic cells of platinum-iron and platinum-zinc couples to determine the time-of-wetness. Time-of-wetness was arbitrarily defined as the interval during which the external potential exceeded 0.2 V. This figure was the period during which the relative humidity was greater than 85% [*12,16*]. Tomashov [*33*] has used sandwich-type galvanic cells of iron-copper, iron-zinc, iron-aluminum, and copper-aluminum. They concluded that the method was suitable for fast determination of the corrosivity of the atmosphere and that the direct measurement of corrosion rate for testing metals was possible.

Several investigators [*17,34–36*] have used galvanic cells consisting of steel-copper and electrolytic cells consisting of individual metals (steel, zinc, or copper) to which an external potential was applied. They concluded that the cell current gave qualitative agreement with the weight-loss data. Recently, extensive studies have been performed by Mansfeld and his coworkers [*30–31,37–39*]. They used galvanic cells and electrolytic cells which consisted of two electrodes and three electrodes. Galvanic cells such as copper-steel, copper-zinc, steel-zinc, steel-aluminum, and aluminum-zinc couples were used to study the effects of pollutants, relative humidity, and so on. They used the electrolytic cells such as two- and three-electrode cells for studies of the corrosion kinetics and for the measurement of corrosion currents. The polarization resistance method was used to determine atmospheric corrosion kinetics under thin electrolytic layers. Mazza et al. [*40*] have used a galvanic cell that consisted of a sandwich formed of bronze covered by its artificial corrosion products on which a high-porosity gold film was applied. They monitored the corrosion current with a zero resistance ammeter and obtained instantaneous and continuous information on the corrosion rate of the bronze. Tosto and Bruco [*41*] used galvanic cells of copper-steel to obtain the relation between the corrosion content and relative humidity. They found that the corrosion current depended on relative humidity (RH).

As a rapid electrochemical method for monitoring atmospheric corrosion, measurements of electrode potential using a suitable reference electrode have been developed by several investigators [*42–43*]. Although the method gives no absolute data on corrosion rates, it is a fast and easy method for on-site investigations. Thin film methods to measure corrosion rates were discussed by Howard [*44*]. Pourbaix and his coworkers [*42,45*] developed an accelerated electrochemical wet and dry method that was designed to use alternate immersion cycles in an electrolyte bath. The electrode potential was monitored when the steel electrode was in the wet part of the cycle. They concluded that their method was selective and yielded reproducible data.

Electrochemical cells designed to simulate thin electrolytic films formed during atmospheric corrosion have been developed by several investigators [*46–47*]. Fishman and Crowe [*47*] have studied the thin film of electrolyte with a potentiostatic polarization technique. The corrosion current increased with an increase of relative humidity. They concluded that the resultant corrosion rates were consistent with those reported from long-term weight loss measurements. Fiaud [*46*] created a thin electrolytic film (80-μm thickness) using the device similar to one developed in the field of thin layer electrochemistry [*48*]. Platinum and nickel were used as electrodes and sodium sulfate (Na_2SO_4) solution was used as the electrolyte with change of pH by addition of sulfur dioxide (H_2SO_4). SO_2 gas was introduced into the electrolyte through a membrane. They observed the depolarization effect of SO_2, oxidation of SO_2, and reduction of SO_2 with use of cyclic voltammetry and linear polarization techniques.

CORROSION OF THIN METAL FILMS AND MICROSTRUCTURES

Corrosion of a metal occurs by the same fundamental reactions whether it is used in a large structure like an automobile, a bridge, or a heat exchanger, or in a small structure characteristic of magnetic, optical, or microelectronic devices, or under a protective layer [*49*]. The uniqueness of each application is tied up in the definition of the environment to which the metal is exposed or which develops with time, as well as the definition of a characteristic size of the corroding material. Since the time to failure of a material (i.e., its lifetime) is normally inversely proportional to the corrosion rate and directly proportional to the thickness of the corroding

material (its characteristic size), small dimensions are more susceptible to corrosion failure and loss of properties. For example (see Fig. 1), a 50-nm cobalt magnetic film may be corroded completely in about 38 h at a corrosion rate of 1 $\mu A/cm^2$. The desired lifetime is about five years, so a protective film (e.g., diamond-like carbon) must be used to moderate the rate of attack. The protective layer must be thin to read or write to the cobalt film with the magnetic head, and defects in the protective layer will lead to localized corrosion attac. Wear and friction are mechanical processes that result from the relative movement of the disk and head. The head is designed to fly very close to the disk to take advantage of the magnetic properties [*50*], but it comes to rest on the disk surface when the system is idle. Humidity and other factors affect wear and friction, and layers or films may be added to lubricate the magnetic film. Of more interest here, however, are the chemical effects that cause corrosion. Accelerated tests have been used to determine disk reliability [*51*], tests that measure the affects of wear, friction, atmospheric contaminants, humidity, oxygen diffusion, and galvanic corrosion. Also described by Antler and Dunbar et al. [*51*] is the comparison between field test experience and laboratory-simulated corrosion test results. Earlier results on microelectronics failures are reviewed by Schnable et al. [*52*], Comizzoli et al. [*53*], Wood [*54*], and Stojadinovic et al. [*55*]. Whatever the mode, the result is a loss of information at the site of degradation and the loss of properties. Better preparation and processing, or better design, may reduce flaws and defects that cause mechanical failure, but they may not reduce corrosion that is the result of the natural instability of the metal in an aggressive environment. Rarely are the thin film metals stable in the environment, so techniques must be found to stabilize the structures and extend the lifetimes.

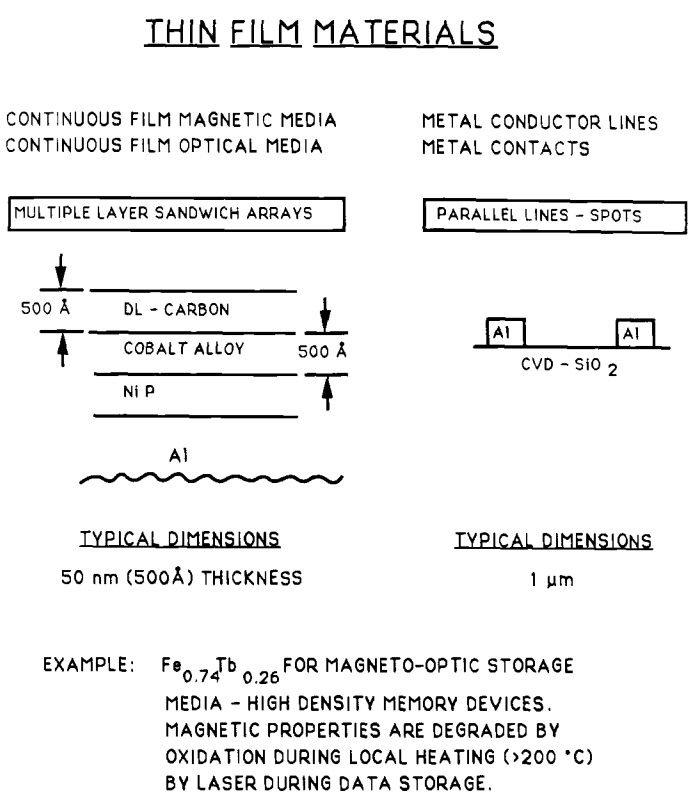

FIG. 1—Thin film materials for magnetic, optical, metal conductor lines and microelectronic contacts make them highly susceptible to have small dimensions are highly susceptible to corrosion.

In the other example of Fig. 1, aluminum interconnects in microelectronic devices have characteristic widths of 1 μm or smaller. Ionic conduction along adsorbed water layers at the silicon dioxide (SiO_2) surface can lead to electrochemical corrosion and "breaks" in the Al conductor. If the corrosion rate were 1 $\mu A/cm^2$, the lifetime of the Al interconnects would be about 48 days, rather than the 10 to 20-year lifetime desired. A protective layer is required for this application as well.

The corrosion phenomena of thin films chosen for magnetic, optical, or electrical applications have unique characteristics, but they are often similar to those observed for bulk materials [*35,50,56*]. Thin films have bulk metallurgical properties in thicknesses larger than 1 to 3 nm and have the same chemical reactions as well. Both observations lead to the general conclusion that both bulk metals and films 30 nm or thicker will have similar corrosion behavior. On the other hand, thin film materials have small grain size and are prepared for magnetic disk applications in "tracked" or grooved geometries. The small grain size causes films to have more homogeneous properties, with fewer inclusions and smaller chemical segregation effects than ordinary bulk materials. The tracks have sharp edges and dimensions to generate unique morphologies in the films. The homogeneous properties would make the films less susceptible to corrosion, but the defects generated at edges could be sites for enhanced attack. The dimensions and geometry of the tracks may lead to nonuniform chemical composition in the recesses, which would produce localized corrosion effects as well. Atmospheric corrosion has been studied under simulated conditions for thin magnetic films [*35*], and, as in other cases, it was found that the affect of humidity and atmospheric pollutants was synergistic. The level of humidity may influence the condensation of thin moisture films on surfaces, which will facilitate transport across surfaces and may cause the accumulation of water in microscopic domains. In the latter, the concentrations of dissolved contaminants may approach saturation conditions. The contamination may come from dust or inclusions of other layers [*49*]. The conditions are difficult to simulate in the laboratory because of the lack of knowledge of local conditions in the microscopic regions that are relevant to the problem. In addition, it has been difficult to make in situ measurements for conditions that simulate atmospheric-corrosion measurements, which would give a direct indication of the processes responsible for corrosive attack. Several standard tests have been developed to assess atmospheric corrosion damage [ASTM Test Method for Assessing Galvanic Corrosion Caused by the Atmosphere (G 104-89); ASTM Practice for Conducting Atmospheric Corrosion Tests on Metals (G 50-76 (1990)); ASTM Practice for Rating of Electroplated Panels Subjected to Atmospheric Exposure (B 537-70 (1992)] without addressing the mechanism of the attack.

The second topic relates to protective layers and encapsulants. Pore-free conventional protective layers over magnetic films are too thick to be compatible with the magnetic properties of thin film disk materials. In addition, poly-

mer films can change the adhesion properties of the surface and interfere with the operation of the magnetic head. Highly resistive but electroactive overlayers could lead to galvanic attack of the substrate through holes in the thin film. Sputtered diamond-like carbon films [*51,57–60*] could fall into this category (see Fig. 1).

A protective layer plated or sputtered over an active metal may have pores and defects that will permit the corrosive medium to contact the active substrate metal and thereby promote galvanic corrosion. The holes or defects may be present on a heterogeneous surface in the geometry of either regular arrays or random arrays. The mathematical modeling of galvanic behavior in plating corrosion systems has been discussed by Smyrl and Newman [*21*], where earlier work was also reviewed. They determined the current and potential distributions of galvanic corrosion system, which consisted of anodic disks in a cathodic plane as shown in Fig. 2. They solved the Laplace equation for potential with nonlinear (Butler-Volmer) boundary conditions with the use of finite difference method. The numerical modeling of galvanic corrosion in which the geometry consists of various array forms has been performed by Morris and Smyrl [*61–63*] in this laboratory. Either regular or random arrays of disks in the cathodic plane were used for the simulation of a heterogeneous surface. Most treatments of the regular array use the symmetry element derived from symmetrical geometry of the system. For mathematical simplicity, a particular hexagonal symmetry element can be approximated by a circular geometry, thus eliminating any angular dependence. For random arrays, the arrays simulated using a Voroni tessellation of the plane into random polygons as shown in Fig. 3 were used for the disk-cathodic plane geometry. The Voroni tessellation has proven to be useful for modelling the transport and mechanical properties of disordered or composite media. The geometrical properties of the Voroni tessellation and algorithms for generating the tessellation have been described by Winterfeld [*64*]. The model established by Morris and Smyrl included the Laplace equation for potential distribution with nonlinear boundary conditions, and it was solved by a finite element method. The potential distribution of the system was obtained from numerical simulation of a regular array of disks over a cathodic plane. The disks were of alternating sizes (disks with two different diameters) distributed on the surrounding plane. The models for the tertiary current distribution, which includes both potential distribution and mass conservation with use of a geometry of the random array, are in progress in our laboratory.

Since the total anodic current must be equal to the total cathodic current, the area ratio between anodic and cathodic components of the total area is an important parameter in galvanic corrosion. If the currents to each area were uniform, the area ratio is the *only* parameter that would affect the galvanic interaction for a particular combination of metals. On the other hand, Smyrl and Newman [*21*] found that ohmic effects in the electrolyte may cause a nonuniform galvanic current distribution on the component areas, and this leads to the conclusion that under such conditions some parts of the cathodic area are not important in determining the total galvanic current. The effect is even more pronounced under circumstances where the electrolyte phase is very thin, that is, galvanic current from cathode to anode flows only near

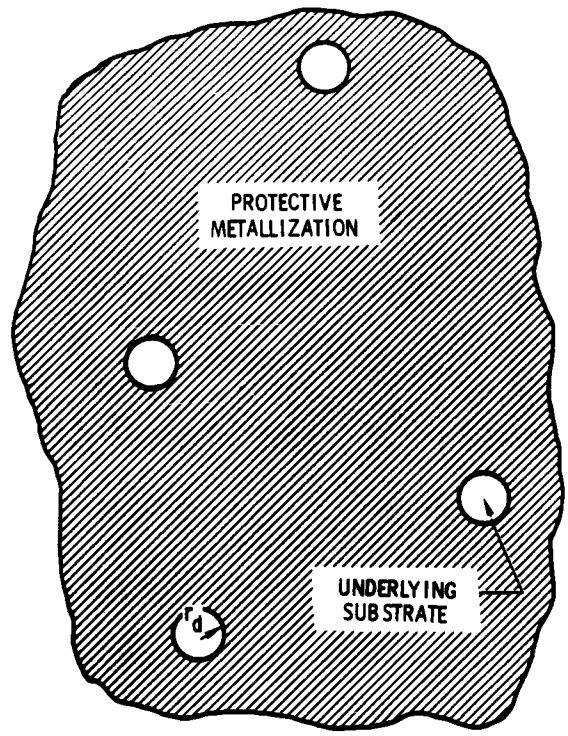

FIG. 2–Multilayer "sandwich" arrays may have underlayers exposed through holes or holidays in the overlayer, and galvanic interactions may enhance the corrosion rate in such systems.

where they join, and more remote areas of each are relatively unaffected by the galvanic coupling. It has recently been found that the *active perimeter* measure of the interactions is more relevant than the area ratio, and the former may be used to correlate the behavior of several geometries [*61–63*]. The nonuniform current distribution is also obtained if the cathodic surrounding plane is highly resistive but electroactive. For example, resistive sputtered carbon films would cause the cathodic galvanic current to flow only to areas at the periphery of holes and defects [*65*], and the total area would not be important in determining the galvanic current. However, smaller holes would increase the galvanic current at a constant area ratio because the active perimeter would increase.

In summary, investigations in bulk solution provide a basis on which to begin to analyze atmospheric corrosion behavior. As the electrolyte phase decreases in thickness, ohmic and diffusion effects become more dominant and galvanic

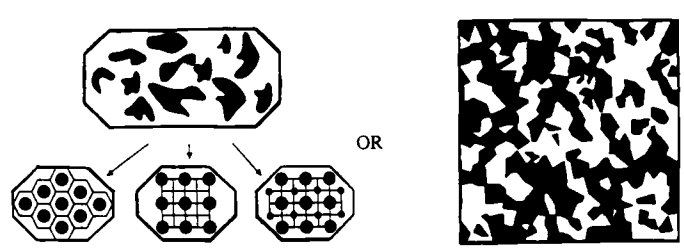

FIG. 3–Simulations of galvanic interactions in multilayer arrays have been carried out with regular patterns or with (more realistic) Voronoi tessellation representations.

coupling is strongly affected. The more remote areas will show the behavior expected for uniform exposure to an aggressive environment. Effects of local composition and local physical geometry then will become more dominant. Behavior in the local areas would be expected to be very similar to the behavior in bulk electrolyte at the same composition conditions. Further general comparisons must be developed as further research is conducted.

COATINGS AND OVERLAYERS FOR CORROSION CONTROL

In the past 15 to 20 years, an explosion of interest in surface modification techniques has mostly involved the deposition of thin films, the application of coatings, and the formation of surface alloys. The development of many of the techniques has been driven by the need for the semiconductor electronics industry to create improved processing procedures. As a spin off of the advancing technology, other fields, such as corrosion protection, have benefited from the new processes. A recent panel report [*66*] has summarized the general surface modification techniques that are used. The techniques are divided into three broad categories:

- Low-energy inorganic coating techniques. For the most part these are mature technologies that have been used for many years.
- Polymer coatings include traditional paints, thermoplastics, poly(vinyl chloride)s, epoxies, urethanes, and poly(methylmethacrylate).
- Techniques involving the use of energetic ions. The techniques have developed rapidly in the last 10 to 15 years; several have neither reached maturity nor found use for corrosion protection. Only those designated as low cost and scalable for widespread use are viable for corrosion protection, except in critical applications. In addition, most techniques that require vacuum processing are too costly for most applications.

Inorganic sol-gel films are formed from a sol through continuous stages of increasing concentration of a solid precursor. Typically, the sol is a solution of polymeric species or a suspension of "oligomers" including particles in the colloidal-size range. During deposition through states of increasing solids concentration, the sol might gel, but the gel state is often a fleeting transient that quickly empties of liquid. Nevertheless, the structures formed during this stage have varying amounts of porosity and influence the structure of the final film. This processing offers good control of composition and homogeneity at low temperatures. It is not directional nor equipment intensive. Complex shapes of arbitrary size can be coated with good uniformity. The cost of high-purity liquid precursors may be high, but for thin-film applications the materials cost would be acceptable.

Films deposited using energetic deposition techniques are dense, highly adherent, have few pinholes, and can be laid down at low temperatures. They are attractive for corrosion protection. Ion-beam-assisted deposition and ion implantation have the best adhesion properties, while RF sputtering has the best throwing power. Three important factors affecting the performance of films are porosity, adhesion, and stress. Although there are compressive stresses, in ion-implanted surfaces, for example, delamination by buckling is practically unknown. Effective porosity in the treated layer could exist due to shadowing of the surface from the beam by contaminating particles. The problem has not been observed, but the exact reason is not known. With the exception of ion implantation [*67*], only a few studies on corrosion have been done on films deposited using energetic deposition methods. Ion-beam-assisted deposition coatings are adherent and more ductile than bulk materials due to the microcrystalline or amorphous structures. The adhesion is better for the films deposited by energetic beam techniques as compared to films derived from physical vapor deposition. More details may be found in the cited report [*66*] or in the original literature.

Polymeric materials are widely used as protective coatings because they are transport barriers which limit access of reactive species (i.e., water, oxygen, ions) to the substrate surface. Leidheiser and Granata [*68*] have discussed the roles that each of these species may play in degradation processes on metal surfaces, and, in particular, the role of ion transport through bulk films and "ion channels" in films. Several techniques are discussed in this paper for characterizing ion transport: d-c measurements, electrochemical impedance analysis, under-the-coating sensing, and radio tracer measurements. Characteristic d-c resistances of 10^{11} ohm·cm^2 are observed for films without continuous aqueous pathways through the coating, as first described by Asbeck and Van Loo [*69*]. The resistance drops to the order of 10^8 ohm·cm^2 if continuous aqueous pathways exist where such pathways have high rates of transport. It is also clear that films and coatings are heterogeneous and the aqueous pathways are surrounded by regions of lower transport rates. The resistance of films may also decrease with time as the ion channels or pathways equilibrate with an external aqueous environment.

For films with high resistance and no ion channels, the impedance of the film is dominated by its geometric capacitance. For films of lower resistance, the low-frequency impedance is dominated by the sum of the resistance of the film and the resistance of the electrolyte. If corrosion proceeds under the coating because of ingress of the aqueous environment, the low-frequency impedance decreases in value. It has been argued that there is a strong correlation between the sites for corrosion under the film and the intersection of the ion channels with the underlying surface, but it has been difficult to confirm the correlation with direct observations.

The nature of the easy pathways for transport appears to be related to several factors. One of the factors is the presence of pigment and filler particles, which could facilitate the formation of aqueous pathways adjacent to the pigment or filler and would be influenced by the interaction of the particles with the polymer matrix [*68*]. The channels could also form by coalescence of voids or pores in the polymer matrix, and this would be influenced by the formation processes of the films. Aggregation of solvent in the film could be influenced by the prior history of the film, by the presence of impurities, and by retained solvent.

The presence of channels has been demonstrated to be a function of the glass transition temperature (T_g) of films as well. That is, below T_g, the polymer will be brittle unless a secondary, low-temperature relaxation exists, and this will favor the formation of microcracks and defects. Above T_g, the

film will be more flexible and less susceptible to formation of fracture channels. Armstrong et al. [*70*] have investigated the influence of T_g on ion transport and permeability in chlorinated rubber films.

Pigment and filler particles can have a beneficial influence because of the reduced transport of water, oxygen, and ions. The effect will depend on the pigment volume fraction, the chemical composition, the geometry, and the dispersion as noted by Burns and Bradley [*71*]. Equilibrium water uptake may cause plasticization and subsequent depression of T_g, as well as swelling, which counteracts the effects of reduced transport rate caused by the solid particles [*72*]. Pigments that have oxidizing character can induce passivation of the underlying metal, as observed for chromate or vanadate additives [*73*]. Other pigments may inhibit the cathodic reaction and thus suppress corrosion as well [*74*].

De-adhesion of organic coatings is responsible for enhanced corrosion rates on one hand and is the result of corrosion on the other hand. Leidheiser [*75*] has discussed de-adhesion processes which include: loss of adhesion when wet, cathodic delamination, cathodic blistering, swelling of the polymer, gas blistering by corrosion, osmotic blistering, thermal cycling, and anodic undermining. With few exceptions, the loss of adhesion processes requires that reactive species such as water, oxygen, and ions penetrate through the coating. Bonds of the coating with the surface of a steel substrate may be attacked by high pH conditions, which are the result of corrosion reactions or imposed cathodic protection conditions. In either case, OH ions are particularly aggressive and cause disbonding on steel. In a recent investigation by Stratman [*76*], disbonding was followed by monitoring the surface potential of a polymer-coated steel surface with a scanning Kelvin probe technique

A recent international meeting [*1*] reviewed the unsolved problems of corrosion protection by organic coatings, described the current understanding of the technology, and outlined some focus for further progress. In addition to the principles of barrier layer transport that have been described above, there was discussion on the effects of: (1) pretreatment of surfaces, (2) the contribution made by surface inhomogeneities of the substrate, (3) the critical size of a water phase which may be responsible for corrosive attack, (4) stress in the film and stress in the substrate, and (5) incorporation of corrosion inhibitors in protective films. Funke [*77*] later summarized the continuing uncertainties that exist in studying corrosion protection properties of organic coatings. Some scatter of behavior is caused by the age and history of the coating—fresh coatings are more susceptible to swelling and changes in composition. Disbonding may initiate at defects, but it may also occur in the absence of holidays or defects. The water that is associated with disbonding could be transported along the surface and not by permeation through the film. Ions may also move along the interface. All these considerations have considerable implications for electrochemical characterization techniques. A review of various types of organic coatings and their applications in various service conditions is provided by Tator [*78*].

SUMMARY

The atmospheric corrosion of metals is one of the most important single problems facing corrosion science and technology. From small nanostructures to large buildings and bridges, coating techniques are being developed to moderate the rate of degradation with some success. The use of low-cost coatings continues to increase as the coatings are made more impermeable and more adherent to the protected substrate. Higher-cost films applied by high-energy methods are finding wider use in critical applications where conventional coatings are inadequate. In all systems where protection is necessary, the early detection of corrosion is desirable in order to plan replacement and maintenance measures and to avoid catastrophic failures. Detection of the presence of corrosion can be accomplished in two ways: detection of the agent that causes corrosion or detection of the results of the corrosion process either on the material of interest or on a specimen of the material. Sensors and monitors are receiving greater attention in accelerated life testing of materials, and eventually they will be developed more widely for operating systems or in portable monitoring systems. The savings to industry and the public at large would be in the billions of dollars if the onset of failure processes could be detected prior to their culmination in a catastrophic event [*79*].

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Natural Weathering

by Lon S. Hicks[1] *and Michael J. Crewdson*[2]

NATURAL WEATHERING DESCRIBES THE PROCESS of exposing materials to the effects of the outdoor environment. Deterioration caused by the atmosphere occurs to all materials placed in an outdoor environment. Natural weathering tests are an extremely important part of the process of determining the aging characteristics of a material. Weathering tests are used to improve the durability of exposed materials.

All materials exposed to the elements deteriorate; the rate and extent of deterioration is dependent upon the material and the severity of the exposure conditions. Weathering tests provide the means to improve the resistance of a material to those factors.

Paint is currently the single most important material tested for its weathering-resistance properties. Paint is used as a decorative item, but equally as important, paint is used as a protective layer. Painted products are found in many varied environments with equally varied effects upon exposed surfaces. Weathering tests offer an initial view of the expected performance of the paint to the environment.

Natural weathering tests are not, however, simply a case of setting specimens out in the sun and watching what happens; a meaningful test involves a more thorough understanding. A number of important factors must be carefully considered when planning and conducting a weathering test: the cause and effect relationship between the weather and the material, the subtle differences in exposure techniques, and the reporting and inspection methods employed. To achieve the most reliable test result, these fundamentals must be appreciated.

HISTORICAL

The origins of natural weathering testing of paints goes back as far as early caveman drawings in the Ice Age. We do not know if these cave dwellers painted on the outside walls, for if they did, the elements would have long since eroded away the evidence. Inside, where conditions are less severe, the paintings have survived tens of thousands of years.

The modern paint era was the catalyst for current weathering tests. Consumer awareness of deterioration propelled the search for more durable products. At the same time, paint manufacturing companies became cognizant of the fact that durable products sell better; thus they have increased their efforts to improve paint durability. At this time, the only testing was "real world," with results being returned from product surveys and consumer complaints.

The idea for exposure fences and racks to expose paint specimens moved the testing to the research and development stage and away from the after market survey. Research into improved coatings were made on specimens before the product went to market, thus reducing the possibility for failures in the marketplace.

In the early 1920s certain climates were noticed to be more severe on exposed materials than others. At the same time, Florida experienced a land boom with increased development; as the number of consumer items increases, it became apparent that life expectancy for these products was much less in the "Sunshine State" than in the Northern Temperate Zone. Prior to this time, natural weathering tests were conducted mostly in the Northeast and Midwest, where the majority of the large paint companies were situated, but the discovery of the faster weathering led several of these manufacturers (along with car companies) to set up their own exposure stations in South Florida.

Also at this time, several independent weathering stations were founded (see Fig. 1) to provide this important service to all companies. The cooperation between independent test stations and paint manufacturing companies over the last 60 years has led to a greater understanding of the cause and effect relationship between the weather and material and also to refining and improving techniques used to conduct weathering tests.

Early weathering tests were almost always at a 45° angle facing south as this was considered the optimum position (see Fig. 2). The fact that most exposure stations in the early years were all in the Northern United States made this even more so. As the focus of outdoor weathering shifted to Florida, realization set in concerning the importance of the angle of exposure and other variables affecting the outcome.

FACTORS OF INFLUENCE

The major influencing factors in the atmosphere involved in the process of weathering are:

1. Sunlight.
2. Temperature.
3. Moisture
4. Pollution
5. Biodeterioration.

[1]Vice president and technical director, respectively, Sub-Tropical Testing Service, 8290 S.W. 120th St., Miami, FL 33156.
[2]General manager/technical director, Q-Lab, 13131 SW 122nd Ave., Miami, FL 33186.

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FIG. 1–Aerial view of exposure site.

FIG. 2–Overview of exposure racks.

Paint will degrade when exposed to the elements in the atmosphere due to the action of these influencing factors, which cause the basic structure to break down. These factors interact synergistically to produce the deterioration of the material we see as a weathering effect.

The relative proportion of each of these factors is important in determining how the overall degradation process will occur. When the factors of influence are changed, so is the degradation produced. Any test method employed to examine weathering must be designed so that the exposure condition is as similar as possible to that of the intended end use of the material. This is the only way accurate predictions may be made concerning the expected life of the material.

An outdoor weathering test is conducted using the natural elements in an uncontrolled environment. Test fixtures and mounting techniques can be chosen to create a similar expo-

sure position as the end use. These techniques include changing angle and orientation, backing type, and the use of specially designed frames to produce a specific microclimate.

The material under test is itself a major factor in the test. The simultaneous exposure of a reference specimen with a known long-term weathering history will ensure that the testing is realistic. If the expected results are given by the reference specimen, there is a greater degree of confidence that the influencing parameters will produce the correct type of changes in the specimen, which is exposed simultaneously.

Sunlight

The effect of exposure to sunlight is the fundamental cause of the weathering deterioration of most materials. The primary component of paint weathering is photodegradation.

Spectral Power Distribution

The wavelength distribution of sunlight that reaches the Earth's surface is important because of the relative effect on the material caused by each wavelength region.

Sunlight can be divided into three major regions: ultraviolet (UV), visible, and infrared (IR). Each region has its own distinct wavelength range [*1*] (see Fig. 3).

1. *Ultraviolet*—wavelengths less than 400 nm.
2. *Visible*—wavelengths between 400 to 700 nm.
3. *Infrared*—wavelengths above 700 nm.

The relative proportion of each of these wavelength regions is shown in Table 1 and described in Fig. 4. The visible region constitutes the largest portion of the overall solar energy; however, it is the UV portion of the sun's energy that is the most destructive element. The ultraviolet can itself be divided into three distinct wavelength ranges [*1*]; only the UVA and the UVB reach the Earth's surface (Fig. 5).

Range	Wavelengths, nm
UVC	less than 280
UVB	280–320
UVA	320–400

There is no UVC at the Earth's surface as wavelengths below 295 to 300 nm are filtered out by the atmosphere [*1*]. The percent composition of the UV regions is shown in Fig. 6. Generally, the shorter the UV wavelength, the more damaging its effect on materials. The UVA and the shorter wavelength UVB are responsible for most photodegradation. Therefore the range of sunlight that comprises the smallest percentage of the solar spectrum is the primary cause for material degradation. This becomes clear when we consider the quantum theory, which describes light as discrete packages of energy called photons. The lower the wavelength, the greater the energy contained in these packets (Fig. 7).

Photodegradation occurs as a result of light energy breaking a chemical bond in the exposed material, causing a deterioration of the physical structure [*2*]. As the wavelengths become shorter, the energy of each individual packet becomes greater, allowing that photon to break progressively stronger molecular bonds. Thus, chemical structures able to withstand irradiation at 350 nm may not be able to endure radi-

TABLE 1—Relative proportion of sunlight wavelength ranges.

Range	Wavelength, nm	Irradiance, W m^{-2}	Percent
UVC	<280	0	
UV UVB	280–320	5	
UVA	320–400	63	6.1
Visible	400–800	580	51.8
Infrared	800–3000	472	42.1
Total	280–3000	1120	100.0

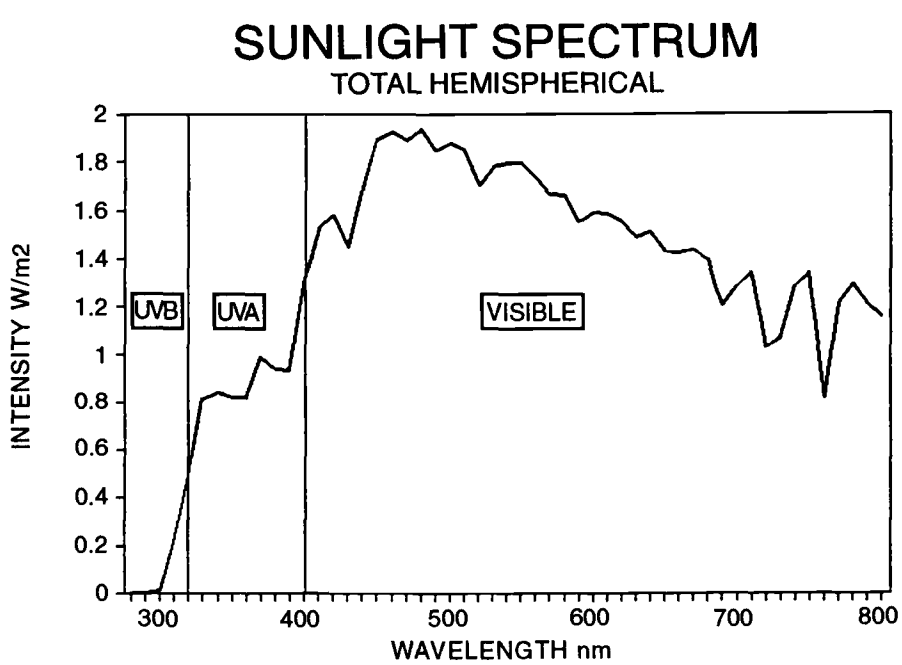

FIG. 3–Solar power distribution, Miami, Florida (solar noon, 26° tilt).

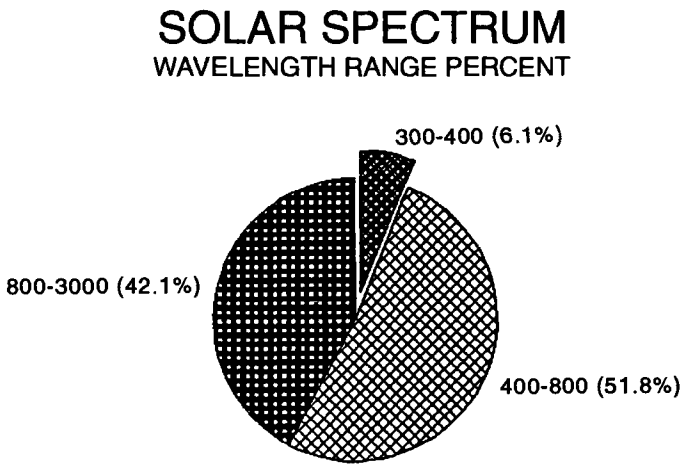

FIG. 4–Percent composition of sunlight.

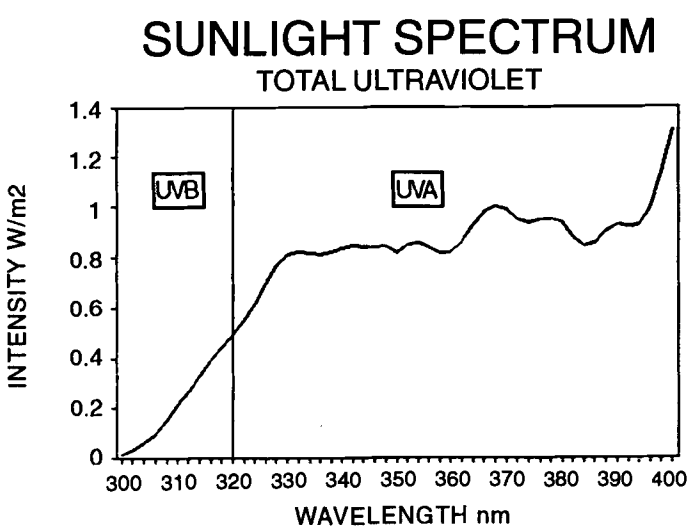

FIG. 5–Ultraviolet spectral power distribution (solar noon, 26° tilt).

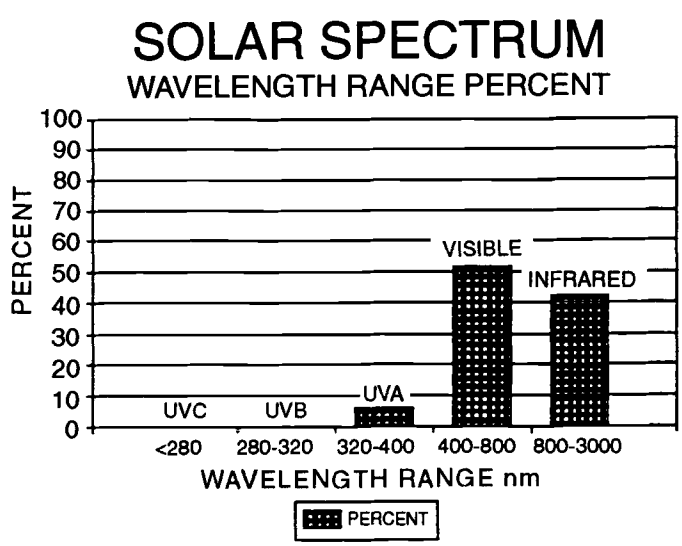

FIG. 6–Percent composition of UV, visible, and infrared.

ation at 320 nm. As the energy level in the photons increases, however, there is a reduction in quantity available. The ultraviolet wavelengths in sunlight contain these high-energy photons. So while the UV makes up only 6% of the total energy, it is that small percentage that causes the damage to occur.

The first law of photochemistry states that only light that is absorbed can cause damage. Thus, if the absorbance of damaging UV energy can be prevented or otherwise reduced, deterioration will be slowed. This premise forms the basis for much of the research in paint formulation.

The visible portion of the solar spectrum is responsible for a limited amount of physical degradation [*3*] and only in a few materials that are susceptible. Some dyes and pigments are sensitive to wavelengths in the lower regions of the visible spectrum. This manifests as color changes in most materials but without changes to other physical properties. Printed materials, paper, and dyes are affected by the visible wavelengths.

The infrared region causes heat buildup to occur on radiated specimens, but has not otherwise been associated with causing significant deterioration to occur. The IR is a factor in the deterioration because absorption of these wavelengths causes specimen temperature to rise, which in turn leads to an increase in the rate of photodegradation.

Radiant Exposure

Exposure to solar radiation causes deterioration to occur, and the more energy absorbed during exposure, the greater the deterioration. The intensity and total dosage of solar energy affect the rate and extent. Daily intensity levels are determined by the season, latitude, and atmospheric conditions of the location [*4*]. A typical day showing total and ultraviolet radiation is shown in Fig. 8.

Radiant energy is monitored and recorded using radiometers. These instruments collect incoming solar radiation from a 180° solid angle, which is identical to the energy collected by the exposed specimens. For more accurate measurement of the amount of radiant energy the paint specimen is receiving, the instrument is tilted at the same angle as the exposure rack.

The integrated total of solar radiation will be the dosage of solar energy on the sample. This total will be affected mostly by atmospheric conditions such as cloudiness: a clear day can yield as much as 30 MJ m^{-2} (approximately 700 langleys) solar energy, whereas a heavily cloudy and overcast day may be barely above zero.

Seasonal Variations

On an annual basis, the dosage of solar energy will change due to the altitude of the sun and the distance between the sun and the Earth [*5*]. This becomes more apparent when the angle of the fixed exposure rack is taken into account. Solar radiant exposure increases when the specimens are positioned at an angle normal to the incident radiation. Therefore, in the summer months in Florida, a 5° tilt angle will receive more energy than a 45° tilt angle. In the winter months, however, when the sun achieves a much lower zenith, the 45° angle receives the most energy [*6*] (Fig. 9). This seasonal difference in radiant energy levels can be seen in Fig. 10.

Over the complete solar cycle of twelve months, a fixed exposure at the same angle as the latitude of the exposure site

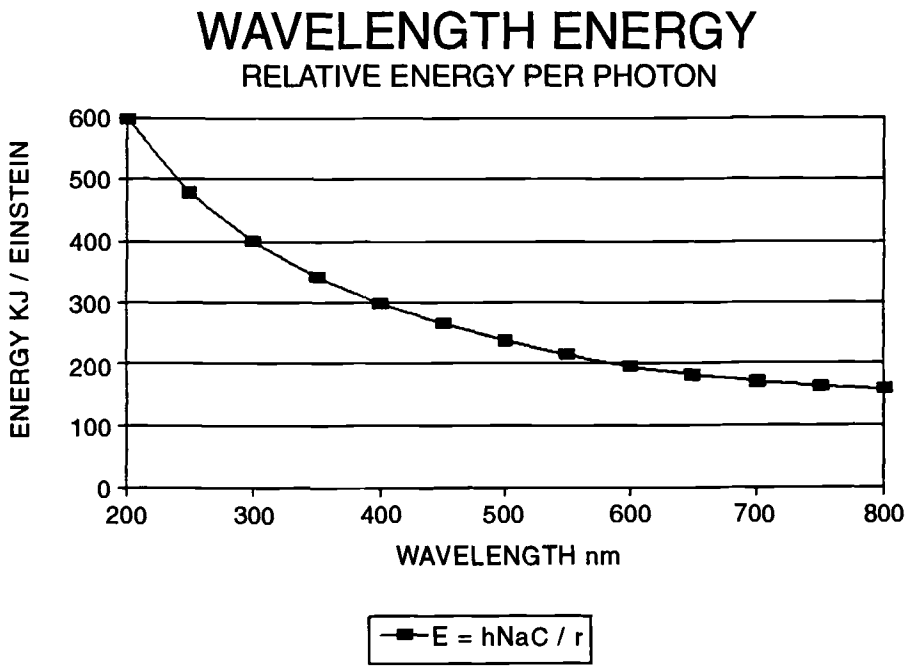

FIG. 7–Energy per photon at each wavelength in sunlight.

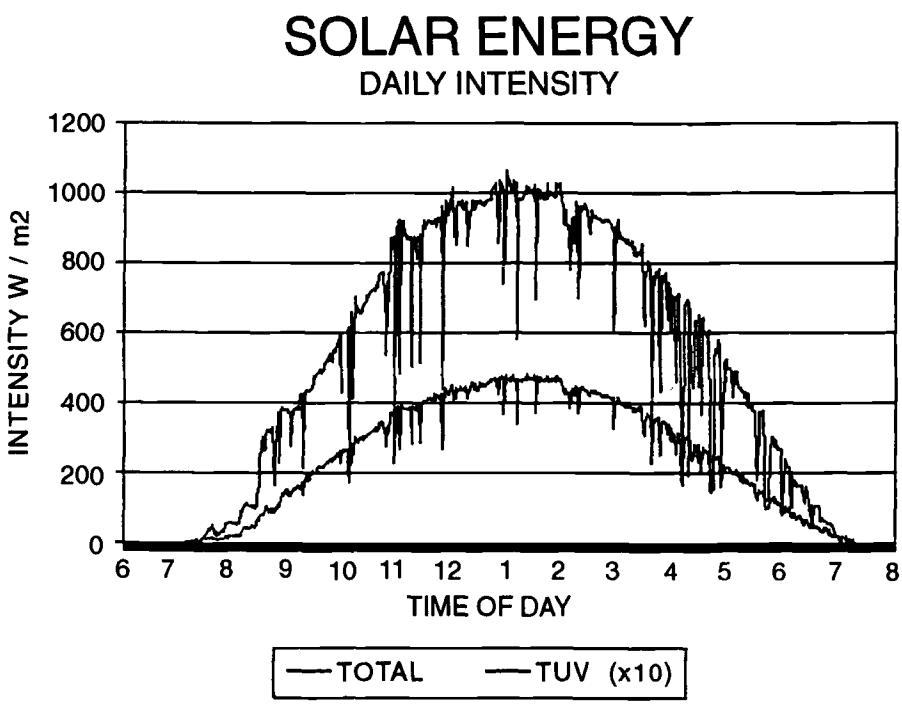

FIG. 8–Daily intensity levels of sunlight, Miami, Florida: Total and ultraviolet, 26° tilt angle. (TUV is shown by the lower line.)

will receive the most radiation, as shown in Table 2. Variable angle exposures where the tilt angle of the rack is changed seasonably to follow the zenith of the sun can be used to increase the radiant exposure by up to 10% depending on location and local climate variability. Short-term exposures, those less than one year, will be affected by seasonal differences in solar energy due to angle of exposure. This important factor must be considered when equating exposure intervals. Timing exposures by amount of radiant exposure will reduce some of these inequities. The use of total ultraviolet energy as a means of timing exposures will further help to even out the seasonal differences in the weathering effect produced. The radiant energy for one year for Miami and Arizona for each of the commonly used exposure angles is shown in Table 2.

Temperature

The temperature of a material on exposure is a primary factor whose influence must be understood in order to relate

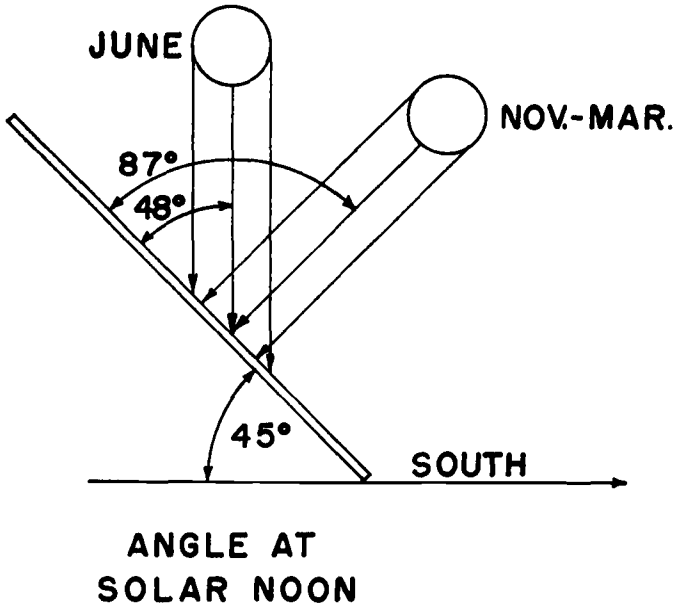

FIG. 9–Angle subtended by sunlight on exposed panel.

the cause and effect relationship of weathering. For most materials, the moderate high temperatures found in service do not cause deterioration per se. However, when the temperature rises in conjunction with solar radiation, the rate and type of deterioration can vary greatly.

In a normal first-order chemical reaction, raising the temperature of the environment by 10°C leads to a doubling of the speed of that forward reaction. However, because material degradation is not a simple one-step chemical reaction, weathering deterioration does not proceed twice as fast when the temperature is raised by 10°C. There is a definite indication, though, that once the breakdown mechanism has been initiated, an increase in thermal load will accelerate the rate of change. A general rule of thumb that has been accepted recently is that an increase of 20°C in the temperature of an exposed specimen results in a doubling of the deterioration rate.

Many chemical reactions have a threshold activation energy, i.e., the temperature level at which a sequence of events will be initiated. Therefore, as thermal input increases, higher threshold levels are surpassed and new mechanisms are initiated. This may cause a change in the overall deterioration produced if the new pathway is significantly different from that at the lower temperature.

It is therefore necessary to conduct the weathering test at the correct temperature. The comparison being made here is that of the actual end use exposure condition to that found in the test method. By having the temperature too low, the rate of change is slowed and deterioration will not be as severe. Conversely, if the temperature is too high, the rate may proceed too quickly and the effect will be more severe.

Paint specimens on exposure derive their temperature from two sources: the ambient air and the radiated infrared from sunlight. The intensity of the sunlight will determine how much higher the temperature of an exposed specimen will be above ambient. Wind speed will assist in reducing the temperatures slightly [7]. The average specimen temperature will show the same seasonal range as that for air temperature (Fig. 11), but will be determined on any given day by the level of solar irradiance (Fig. 12).

The angle of exposure, paint color, and season also contribute to determine the actual temperature at any given time. Thus the specimens are generally hotter during the day than at night, in the summer than in the winter, and on a sunny day rather than on a cloudy one. On any given day, the tem-

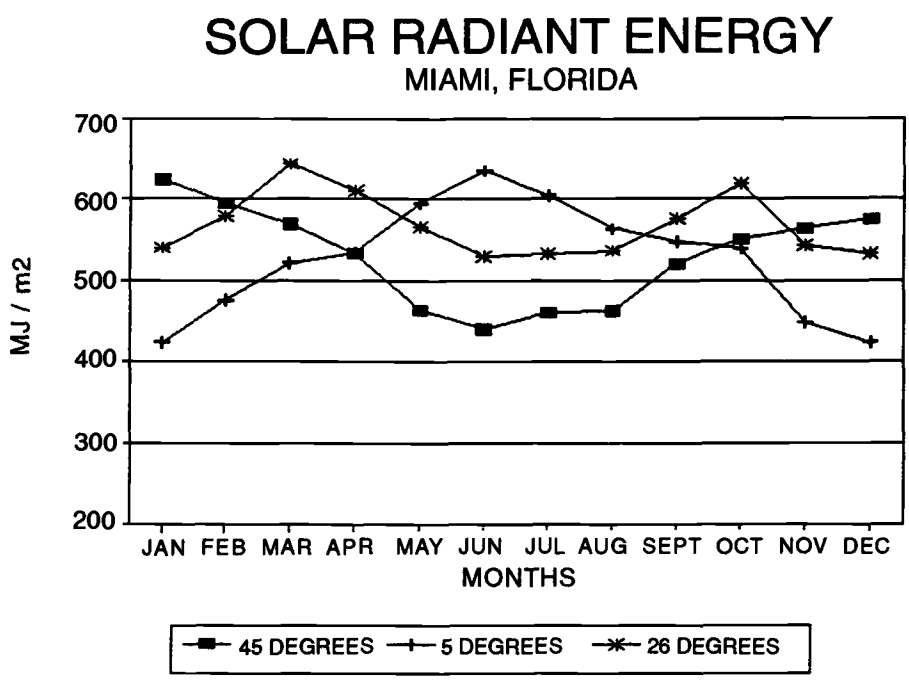

FIG. 10–Seasonal variations in solar energy measured at different fixed angles of exposure.

TABLE 2—Solar radiant energy, average 1990–1991.

Month	Solar Radiation, MJ m^{-2}, Angle of Exposure			
	45°	5°	26°	VA°
January				
Florida	556.79	420.48	514.34	556.79
Arizona	612.50	425.49		
February				
Florida	587.50	483.37	618.09	587.50
Arizona	607.94	476.40		
March				
Florida	601.51	569.90	661.61	661.61
Arizona	631.54	601.35		
April				
Florida	545.76	573.12	623.35	573.35
Arizona	724.23	784.77		
May				
Florida	468.30	600.77	577.21	600.77
Arizona	735.51	897.85		
June				
Florida	441.17	589.38	529.25	589.38
Arizona	648.94	856.13		
July				
Florida	434.21	566.95	531.66	566.95
Arizona	649.66	830.43		
August				
Florida	475.86	572.30	557.65	572.30
Arizona	684.23	774.86		
September				
Florida	475.00	502.78	526.62	526.62
Arizona	658.02	647.56		
October				
Florida	545.50	500.14	561.06	545.60
Arizona	712.30	596.29		
November				
Florida	522.87	425.90	509.88	522.87
Arizona	669.54	471.38		
December				
Florida	524.10	394.72	492.33	524.10
Arizona	601.06	400.22		
Total				
Florida	6178.55	6199.76	6703.02	6827.51
Arizona	7935.44	7762.70		

NOTE: VA = variable angle.

perature of an exposed paint sample will follow closely the irradiance level of the sun. The temperature of the exposed material can be manipulated even in an outdoor exposure test; these techniques are discussed later in "Accelerated Natural Weathering."

Moisture

Water is a primary factor affecting the deterioration of exposed materials. In conjunction with solar radiation and high temperatures, the moisture content in and surrounding an exposed sample is very important in determining the weathering response of that material [*8*]. The presence of water falls into two categories:

1. Gaseous.
2. Aqueous.

Relative Humidity

The gaseous phase is that which describes the moisture content of the air. The amount of water vapor contained in the ambient air is the *absolute humidity*. Warm air is able to hold more water in the vapor phase than cold air. The relationship between the actual moisture content of air and the maximum content at any particular temperature is the *relative humidity*. When the air is fully saturated, the relative humidity is 100%.

Any material placed on exposure will endeavor to maintain a moisture content equilibrium with its surroundings [*9*]. Physical stresses are created as the material loses or gains water content in order to equilibrate, as can be seen in Fig. 13. The greater the range of humidity in the enveloping atmosphere, the greater the overall stress on the material. Because moisture is a major factor in the synergistic effect of weather on exposed materials, a higher moisture content will contribute to increased degradation more than will lower moisture levels. A relative humidity value of 70% is considered the critical threshold for corrosion [*10*]. This indicates that a constant cycling of humidity levels at high values increases the rate of deterioration.

Rainfall

The effective source of visible surface moisture has two origins, and they each have a different effect on the exposed material. The distinction between the two types must be clearly understood.

Rain is an external source of water that is applied to the material via the surface layers. As most rainfall is of short duration, this effect is primarily at the surface and does not play a direct role in the deterioration of the bulk of the material.

Rainfall has the greatest influence at the surface and is responsible for washing away surface layers during periods of heavy rain. For example, rain assists in increasing the rate at which a specimen may chalk, but may also help to remove surface attachments such as dirt and mildew.

Rainfall will cause a thermal shock on exposed specimens, which can be severe in certain circumstances. When the rain occurs at a time when the material is heated from radiant exposure, the cooling effect causes a rapid drop in the temperature of the specimen. This thermal shock can cause mechanical stress as the specimen contracts. In the summer in

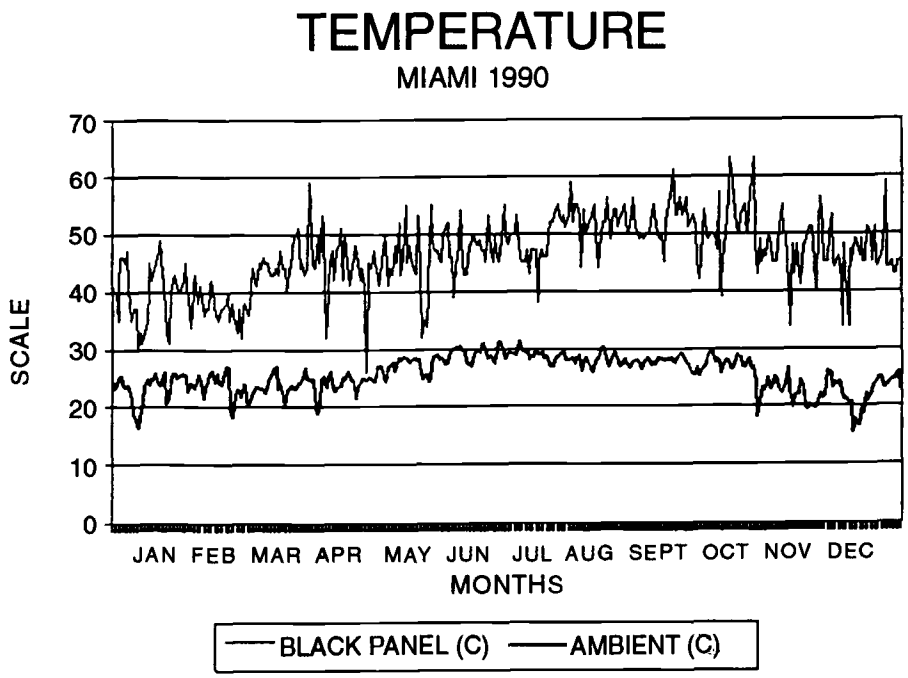

FIG. 11–Daily maximum black panel versus ambient temperature. (Lower line equals ambient temperature.)

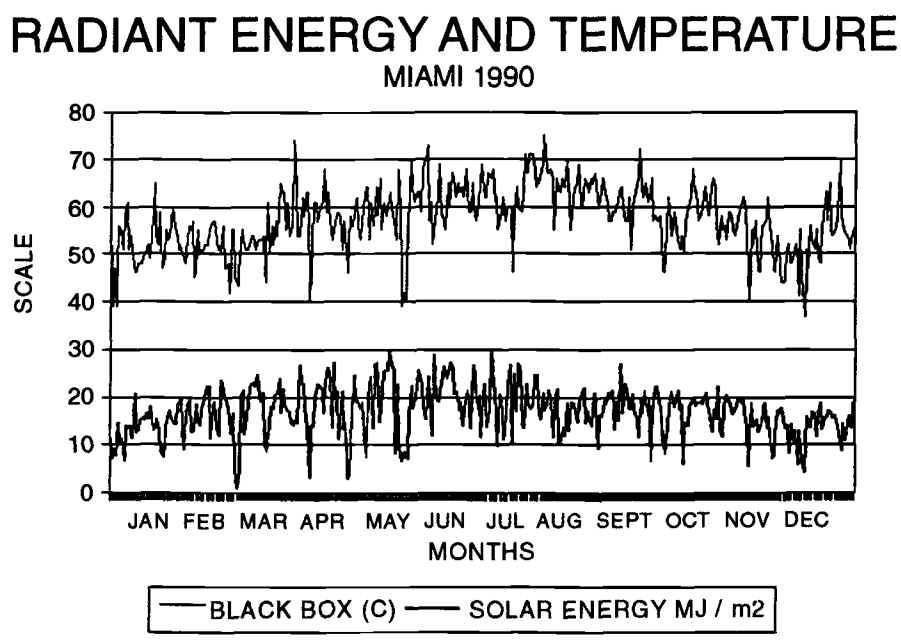

FIG. 12–Daily maximum black box temperature versus daily solar radiant energy. (Upper line equals black box temperature.)

Florida, the temperature of a black panel can drop from 70 to 25°C in about 2 min.

Condensation

Condensation arises when the sample temperature drops below the dew point temperature of the surrounding air. This causes water vapor in the air to condense on the material. The physical and chemical responses of the material caused by condensation have a far greater effect on the material than rainfall. The condensation effect can also be apparent at much deeper levels within the material. Condensation moisture has high levels of dissolved oxygen, which accentuates photodegradation by taking part in the chemical reaction.

The total amount of time a sample is wet is an extremely important factor in the determination of the degree and rate of degradation. Prolonged exposure to surface condensation will allow the absorption or permeation of a relatively high level of water and oxygen, and as the day progresses a strong pressure will be exerted by the atmosphere for water desorption. The longer the intervals of wetting and drying, the

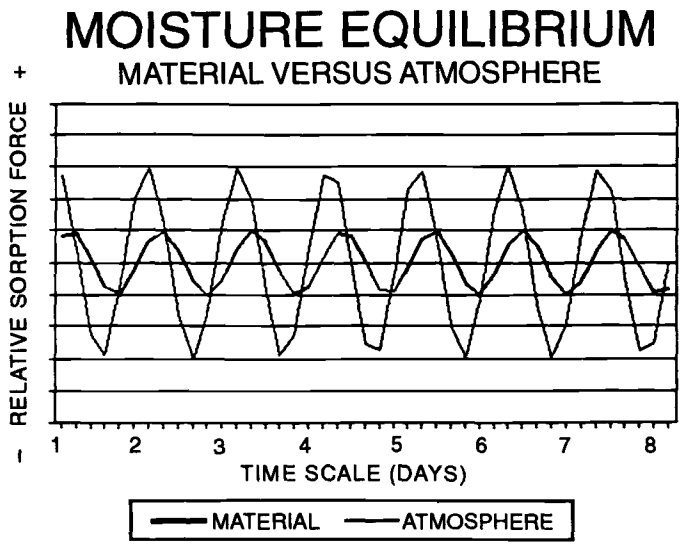

FIG. 13–Ambient versus sample moisture cycling.

deeper into the material will be the cycling effect. Water absorption and desorption rates are also a function of the diffusion coefficient of the material. The faster the rate of cycling, the more the effect remains at the surface and the less penetration is made into the bulk of the material.

The photochemical degradation mechanism is also accentuated by the presence of moisture. Rates of deterioration are greatest when the solar radiation is present in conjunction with high moisture levels. It follows, therefore, that surface breakdown effects such as chalking will occur due to rainfall, condensation, and sunlight interaction, whereas bulk substrate deterioration such as cracking is due in large part to the synergistic effects of humidity, condensation, and temperature, causing mechanical stress and release of strain in the paint film. As surface layers break down, more of the interior bulk of the material is exposed as a new surface layer.

The role of moisture in exposed material breakdown is very important, but it is also important to know the source of the moisture. The different physical (and chemical) effects produced will differ with each source. A climate such as Miami's (Fig. 14), with a range of high humidity and a high percentage of total wet time (approximately 50%), will allow moisture to play a full part in the weathering process [*11*].

Pollution

Atmospheric pollution is a significant, but lesser part of the overall weathering effect. Industrial emissions consisting of compounds that mix with water to form acid rain cause chemical reactions to occur on exposed materials. The severe long-term effect of pollution on even durable materials can be seen by the effect on ancient monuments and statues, which have withstood centuries of exposure only to succumb in recent years to atmospheric contaminants. Short-term exposure to pollution can be just as severe if the material is susceptible.

Pollution is a powerful influence on paint durability, but its effect is difficult to control and monitor. Analysis of the atmosphere will reveal the constituents of the pollution, and comparison to exposure in a clean pollution-free atmosphere will show the additional effect of the pollution on overall weathering.

Although pollutants may directly affect the paint independently of other weathering factors, most often the changes do not occur until the other influences are present. Changes in paints on exposure in industrial areas, which are seen in a relatively short time but which do not show changes in rural areas, are a clear indicator of the effect of the pollution.

Solar energy can act to change the chemical structure of the emitted waste product; for example, atmospheric SO_2 in water does not become sulfuric acid until radiated. The sulfuric acid then causes a color change due to reaction with the pigment.

Large-scale pollution such as the effect of acid rain is felt throughout most of the northeastern United States, with the greatest effect in Pennsylvania, New Jersey, and New York. Acid rain resistance can be included as part of the routine testing procedure by exposure at known polluted sites. The effect is known and is widespread.

Local pollution problems such as the smog in Los Angeles create a problem for the testing industry. Because the chemical effect of each emission is different, the weathering result of a single material may vary from city to city depending upon the industrial base.

Biodeterioration

The phenomenon of material degradation due to attack by biological organisms can take many forms. The most common form of biodeterioration of specimens exposed outdoors in Florida is mildew. The organisms that constitute mildew are fungi, which are individually microscopic but can be seen with the unaided eye when grouped in colonies or having threaded structures called hypha. The spores of the fungi attach to the surface of the material, using the constituent chemicals at the surface as a food source. All fungi are characterized by their inability to synthesize their own foods from carbon dioxide and water. They must therefore utilize an external supply of carbohydrate as their energy source. The exact chemical nature of that source will vary for each fungal species, but the more opportunistic species can use the paint directly.

As the mildew grows, surface conditions are altered. Breakdown products are formed that can act as a food source for a second fungal species, which will find the surface of the paint a favorable place to live. This succession of different organisms constitutes the microecology of the painted material's surface [*12*]. The complicated natural order that occurs in mildew attack on exposed products makes it very difficult to ascertain which species is causing the most damage.

Real-time exposure testing outdoors in conditions favorable to growth is the only way to truly test the mildew-resistance properties of any product. Single culture testing of mildewcides and mildewstats are useful as a preliminary test only.

The subtropical region of Florida is used extensively for the evaluation of fungus growth. The warm, wet climate promotes rapid growth on unprotected materials, with visible hyphae present in just a few days. A number of different exposure methods are employed to study mildew growth, the most common being a vertical north orientation. This gives a

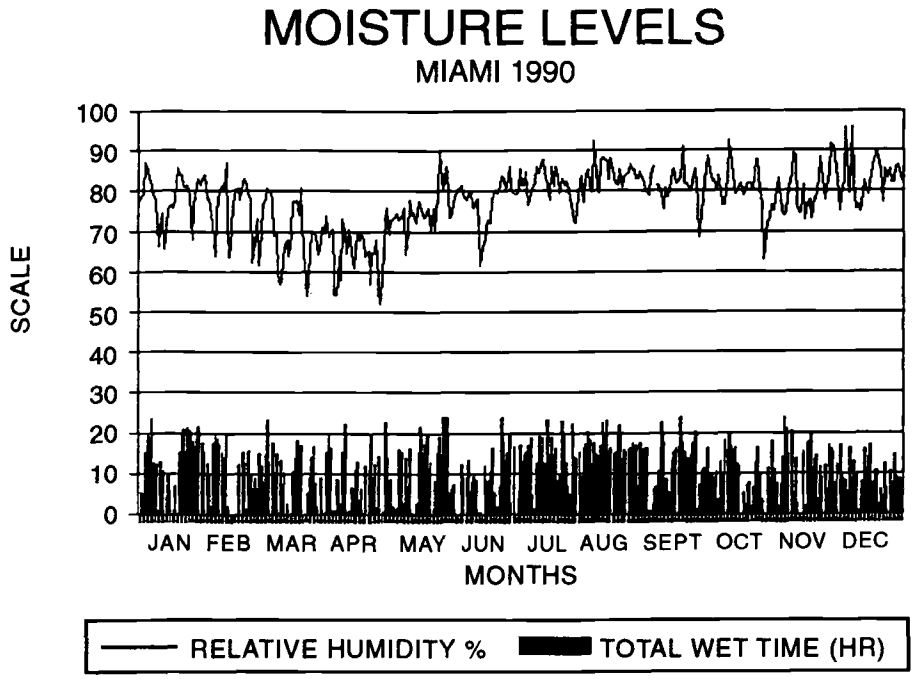

FIG. 14–Daily maximum humidity and total wet time.

shaded, damp location without the natural mildewstatic effect of solar UV radiation. A vertical south position is also used to study mildew growth as part of the total deterioration mechanism. Exposure under a roof overhang is commonly used (Fig. 15), and a tropical forest exposure is the most rigorous example of natural exposure conditions.

Mildew organisms thrive in the damp conditions found in subtropical-type climates, and growth is greatest during the summer months when rainfall and ambient relative humidities are at their highest level and temperatures are 20 to 30°C. Growth is slowed when average daily humidity drops significantly below 70%; however, during the winter, steady growth will still occur on northern exposures and in tropical forests, where moisture levels are higher and temperatures are in the optimum range.

Algae as a biodeterioration factor is different from mildew. Algae is a green plant and able to synthesize food from sunlight, carbon dioxide, and water. Its attachment to paint surfaces is not an actively attacking one as is the case with mildew. The paint film is merely supplying a substrate for the algae. By its presence on the surface, however, algae affects the microclimate and resulting deterioration may occur.

CLIMATOLOGY

Natural weather exposure testing of paints and coatings is conducted at many different sites, each with its own distinct set of influencing factors. It is the combination of the weathering factors that causes the deterioration particular to that location.

As indicated earlier, paint exposure testing facilities are located in many areas, but the subtropical area of Florida is regarded by the United States and by much of the rest of the world as the primary benchmark testing climate. This is because the exposure consists of all of the major environmental parameters in high quantity except pollution.

Each climate type has its own distinct characteristic pattern, which derives from the range of influencing parameters at that location. These can be measured and examined to determine the relative importance of each. Several important climatological types used in weathering are described below.

Climatological Types

Subtropical

The subtropical climate of southern Florida is recognized worldwide as the primary benchmark testing location. It is the climate to which all other locations are inevitably compared. It is no accident that this area is as important as it is, for it is the only true subtropical region within the United States. Due to the historical considerations discussed earlier, Florida is accepted worldwide as the standard in natural weathering. The great majority of materials will fail faster in Florida than anywhere else because the climate contains all of the major influencing parameters except pollution and in relatively high amounts (Fig. 16). The factors act together synergistically, each one increasing the effect of the other.

The high temperatures and humidity complement the photodegradation from solar radiation. The sun's energy is more potent as there is a greater relative proportion of UV to total energy. The time of total wetness is close to 50% of the total time, thereby ensuring a constant cycle of wetting and drying.

Desert

The desert of the Southwest United States (especially the Phoenix area) has also come to be regarded as a primary weathering testing site. Exposure conditions in the desert are very different than in Florida. The desert is widely used because the climate consists of clear skies and prolonged un-

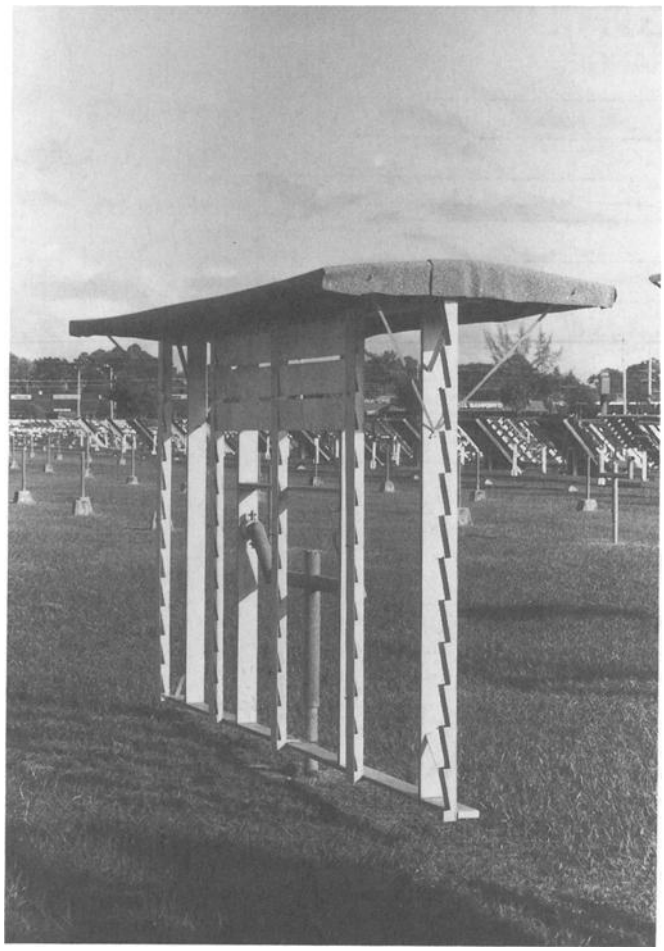

FIG. 15–Vertical exposure under roof.

interrupted solar radiation. High temperatures are produced on exposed materials, and there is a higher absolute dosage of solar UV than in Florida (Fig. 17).

For most materials, however, especially paints, the greater solar UV does not produce faster deterioration than in Florida. This is due to the lack of moisture in the exposure. Without moisture cycling, the effect of temperature and UV is much reduced. There is also no biodeterioration and no corrosion associated with desert exposure.

Extreme Cold

At the opposite end of the exposure scale from the desert is exposure testing in extreme cold weather. Low temperatures are accompanied typically by lower sunlight. International Falls, Minnesota is used as an exposure site for cold weather testing because this area frequently records the lowest temperature in the continental United States (Fig. 18). Cold weather exposure is used to test for specific failure types: cold cracking and freeze thaw deterioration. As the temperature passes through the freeze threshold, any water on the surface or in the bulk of the material forms into ice crystals. As the water freezes, its volume increases by approximately 10%, which is enough to create a substantial physical force on the paint film. This is the one environmental factor that cannot be examined during natural exposure testing in southern Florida.

Temperate with Pollution

Exposure in an industrial environment will indicate whether a paint is susceptible to atmospheric pollution. There are many sources of pollution emission into the atmosphere, and the method of administration to the paint is usually by washout during rainfall. In the United States the geographic area most affected by acid rain is the Northeast, with the next most severe area covering most of the rest of the East and the Midwest [*13*]. It is no coincidence that this is the industrial heart of the country.

The U.S. paint industry has long used Louisville, Kentucky as a typical temperate industrial exposure (Fig. 19). As a large paint manufacturing center, this area has become accepted as a location for exposure to acid rain. The temperature continental climate can be as severe as Florida, but only for a short period during the summer when the temperatures are high, humidity increases, and sunlight levels are similar to the subtropics.

Rainfall pH values below 4.5 have been recorded in some areas of Pennsylvania and New Jersey, as shown in Fig. 20. Paints and other exposed materials used in this area must be made to withstand this acid rain effect. This can be tested in Florida by artificially adding the acidic solution to the outdoor exposure test; however, outdoor exposures should be conducted in the actual polluted environment to best determine resistance.

Marine

Marine Atmosphere—Exposure to a marine atmosphere adds the corrosive influence of salt spray. Predominant test sites are located on the coasts of Florida, New Jersey, North Carolina, Texas, and California. The salt aerosols in the atmosphere settle on the exposed panel and work to enhance rusting. The closer to the surf, the greater the percentage of salt in the atmosphere. A marine atmosphere test combines the natural weathering of the site's climate with the additional natural corrosivity of the sea salt.

Marine Immersion—Exposure in seawater is used to test antifouling paints and rust-protective agents. Two exposure possibilities exist: floating immersion and fixed exposure. The floating rack positions the panels either completely or partially immersed; the level remains the same through each tide cycle. The fixed exposure in the tidal zone causes the panels to be alternately submerged and dry.

Climate Affects Exposure

Weathering deterioration is a function of the material's reaction to the influencing parameters. The two primary testing locations are both located in hot, sunny climates that produce accelerated deterioration compared to most of the rest of the United States. If different climates produce different exposure results, there is a possibility that exposure to only one set of conditions will not reveal the deterioration that may occur in another set [*14*].

Paint deterioration is determined by a number of mechanisms, each with its own threshold level for initiation. There is a level for each of the influencing factors at which the paint

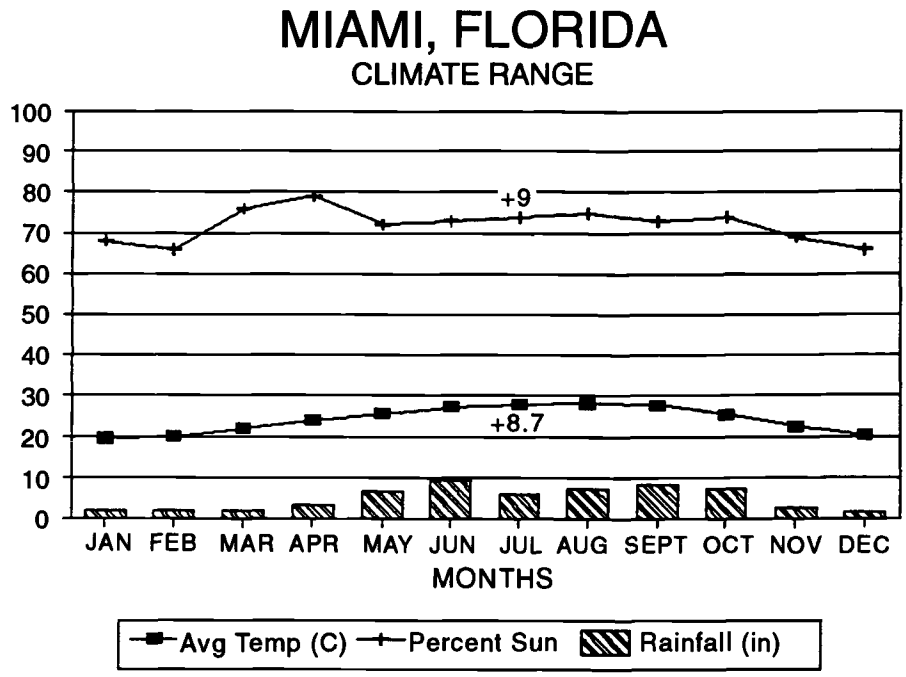

FIG. 16–Climate summary, subtropical (Miami, Florida).

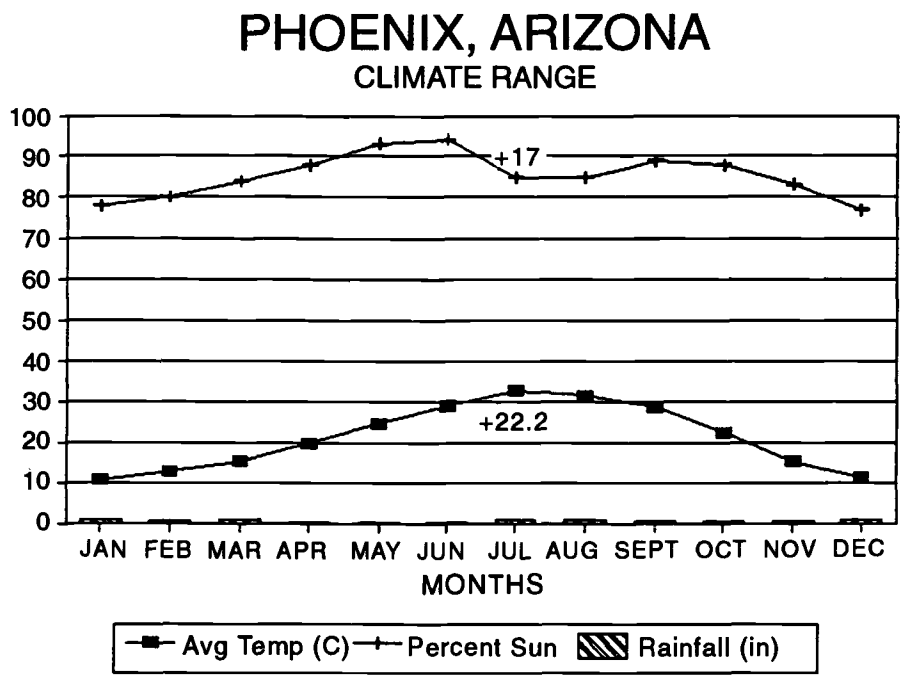

FIG. 17–Climate summary, desert (Phoenix, Arizona).

will become susceptible. When the factors interact, the overall influence is a complicated matrix that is constantly changing.

Degradation is the result of the material's response to its environment. When the environment changes, so do the changes that occur in the material. This does not always manifest as a slower or faster response, but also perhaps as a different one. Generally, however, it is practical to consider Florida as the most severe climate because it has all the influencing parameters in high abundance all year round. Other climates are missing one of the factors or are reduced in effectiveness due to the winter season.

Instrumentation

The atmospheric data required for weathering testing go above and beyond that given by the National Weather Service. The factors affecting material durability must be monitored to understand the cause and effect relationship between paint and the atmosphere. An exposure station weather re-

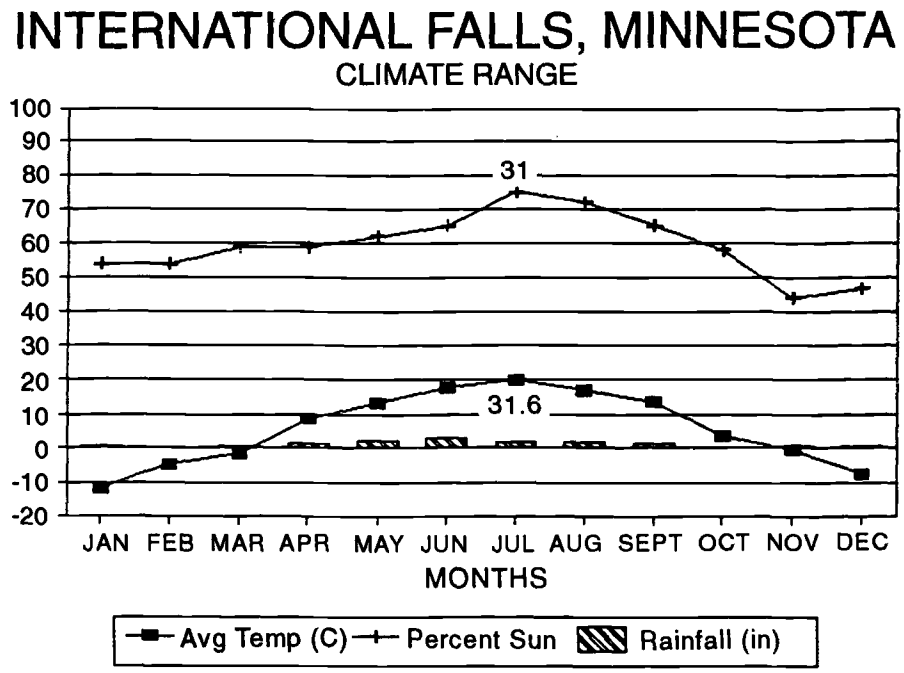

FIG. 18–Climate summary, extreme cold (International Falls, Minnesota).

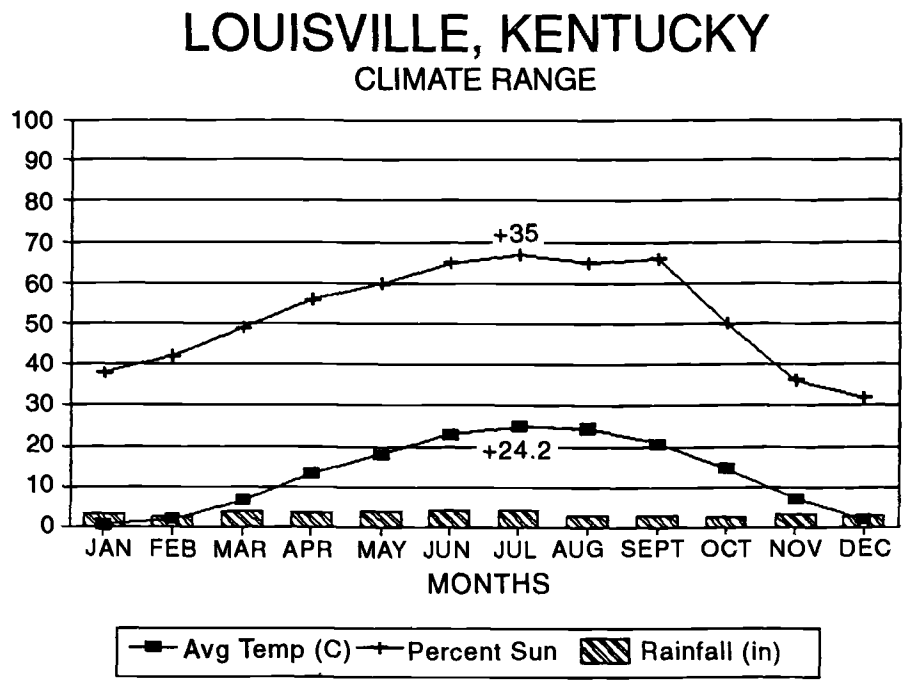

FIG. 19–Climate summary, temperate (Louisville, Kentucky).

port comprises information relevant to the exposed specimen.

The major additional items reported are the solar energy, black panel (or specimen) temperature, and total time of wetness. These are the most relevant atmospheric measurements concerning material exposure. Table 3 lists several parameters and equipment used to collect the information.

As discussed earlier, for weathering requirements, the total solar radiation is measured using a pyranometer, such as the Eppley Precision Spectral Pyranometer (PSP) (Fig. 21), which is sensitive in the range of 300 to 3000 nm. The ultraviolet is measured using a sensor that is sensitive in the range of 300 to 400 nm. The widely used Eppley Total UV Radiometer (TUVR) (Fig. 22) has a sensing range of 295 to 385 nm. These "total" sensors collect incoming radiation from all angles, having a 180° sensitive diffusion cover. This is termed *hemispherical radiation.* Total radiation measurements include both the direct beam from the sun and the diffuse energy from the atmosphere [*15*]. Direct beam radiation, excluding the diffuse sky, is measured with a pyrheliometer such as the

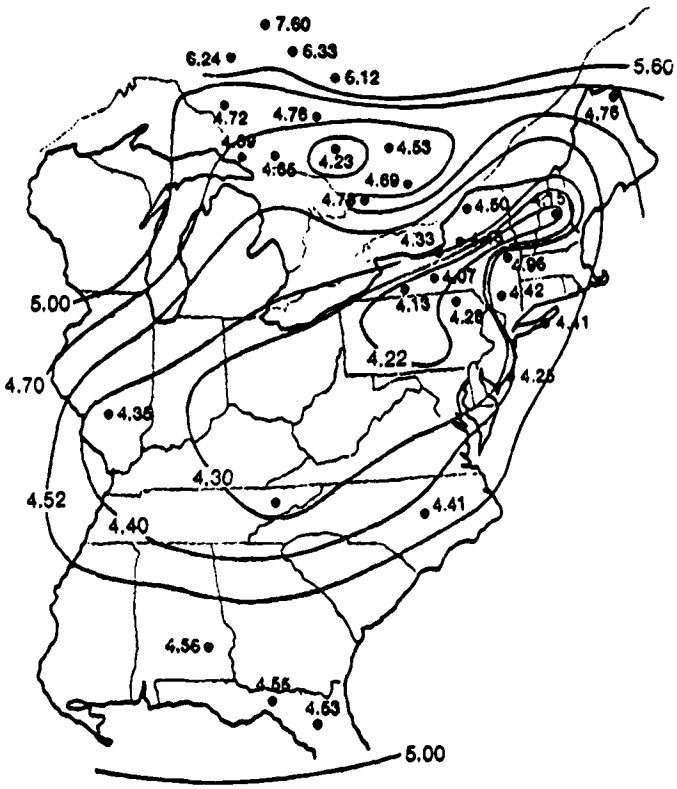

FIG. 20–Precipitation pH in northeastern United States.

TABLE 3—Weathering instruments and sensors.

Measured Parameter	Equipment Used
	Solar Energy
Total hemispherical	Pyranometer (hemispherical) PSP
Total ultraviolet	UV Radiometer (hemispherical) TUVR
Normal incidence	Pyrheliometer (6° solid angle) NIP
	Temperature
Ambient	Thermometer
Black panel	Black panel sensor RTD probe
White panel	White panel sensor RTD probe
Sample temperature	Thermocouple attached to panel
	Moisture
Rainfall amount	Rain gage
Rainfall duration	Heated wetness sensor (impedance)
Total wet time	TOW sensor (impedance)
Relative humidity	Psychrometer or hygrograph
Wet bulb temperature	Thermometer (in wick)
	Miscellaneous
Wind speed	Anemometer and wind vane
Salt aerosols	Wet candle
Sea water temperature	Floating thermometer
Air quality	EPA measurements

NOTE: All sensors should be connected to continuously monitoring and recording devices, e.g., computer-controlled data acquisition system.

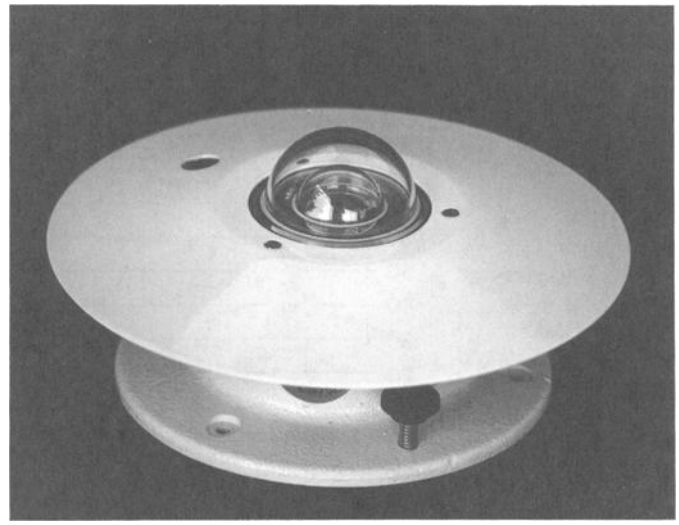

FIG. 21–Precision spectral pyranometer (PSP).

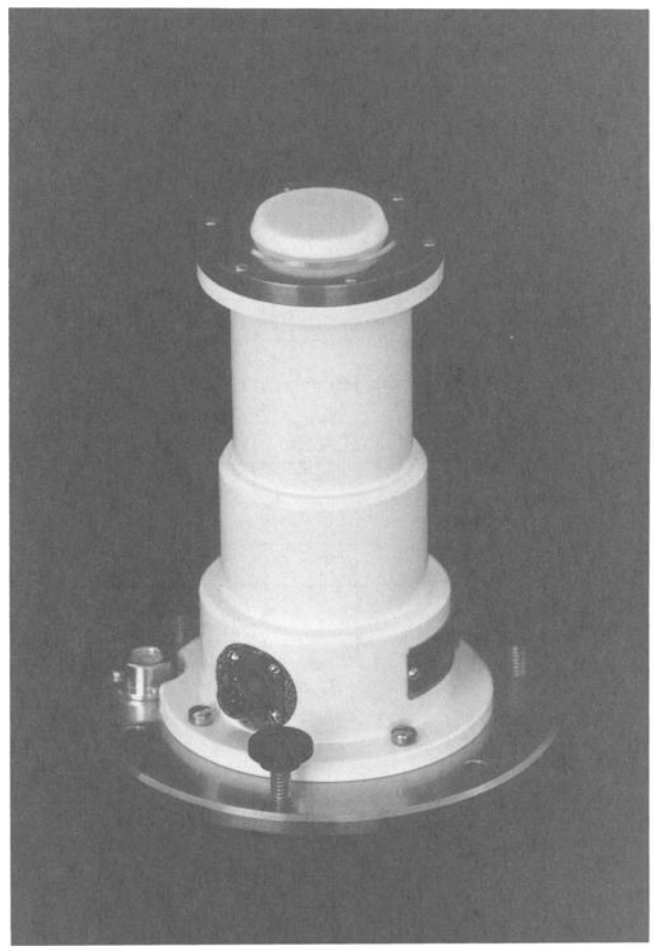

FIG. 22–Total ultraviolet radiometer (TUVR).

Eppley Normal Incidence Pyranometer (NIP). This has a 6° solid angle field of view and measures from 300 to 3000 nm. To work correctly, it must be mounted on a solar tracking device.

The intensity of the radiation is integrated with respect to time, thus allowing the amount of radiant exposure to be calculated. Values for radiant exposure are given in megajoules per square metre (MJ m^{-2}). This is the recom-

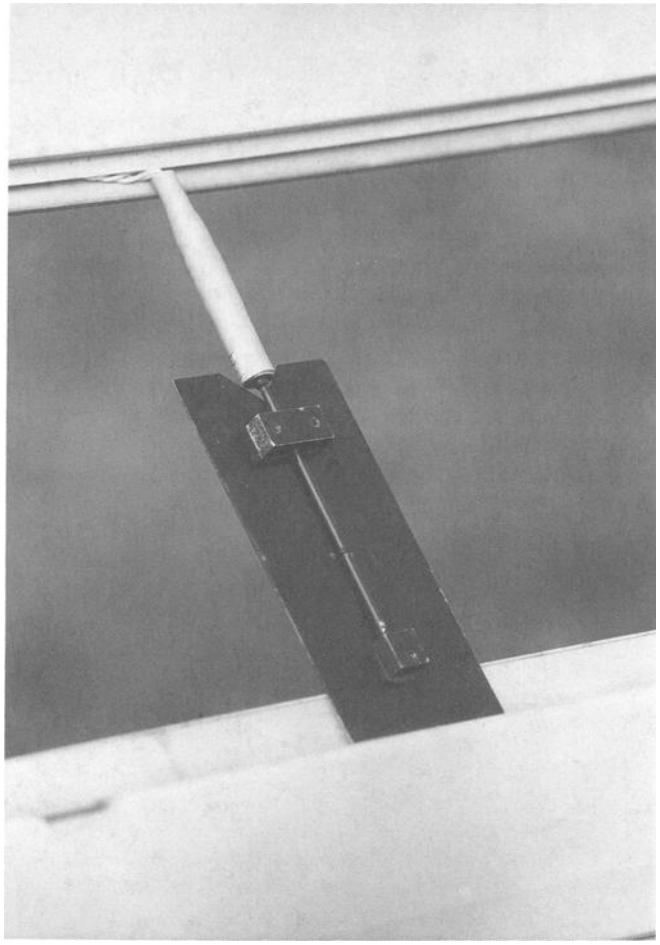

FIG. 23–Black panel thermometer.

mended SI unit; an older term used for these values is the langley, which is 1 calorie per square centimetre (1 cal cm^{-2}). To directly convert langleys to megajoules, multiply the langley amount by 0.041 84. This accounts for both the conversion from calories to joules and the change in unit area.

Black panel temperature is a measurement widely used in weathering exposures, both natural and accelerated. It is the surface temperature of a black-painted metal panel (Fig. 23) and is used to obtain a reference temperature for a paint panel exposed to a radiant energy source. Exposed materials absorb infrared energy from a light source, which causes their temperature to rise above that of the ambient air temperature. A black panel measurement is the expected maximum temperature a colored panel might achieve when exposed to a particular energy source since black absorbs all light energy. This temperature value is thus an indication of the actual exposure temperature, which is more relevant than air temperature. The black panel temperature will follow the light intensity output level of the sun.

Total time of wetness is the accumulated time an exposed paint panel has visible surface moisture [*16*]. The two sources for this are rainfall and condensation. Surface moisture can be measured by using a sensing element that requires water to complete an electrical circuit, thus operating a recording device. This will record the accumulated time for both rainfall and condensation; the time for rainfall can be removed to obtain the time due to condensation only. The sensor is described in more detail in ASTM Practice for Measurement of Time-of-Wetness on Surfaces Exposed to Wetting Conditions as in Atmospheric Corrosion Testing (G 84).

A rainfall duration sensor (Fig. 24) measures only the wetness time due to precipitation. The sensor is essentially the same as for total wetness measurement except that a constant heating element is incorporated so that any surface moisture will evaporate quickly, switching off the sensor very shortly after the rainfall has stopped. Keeping the tempera-

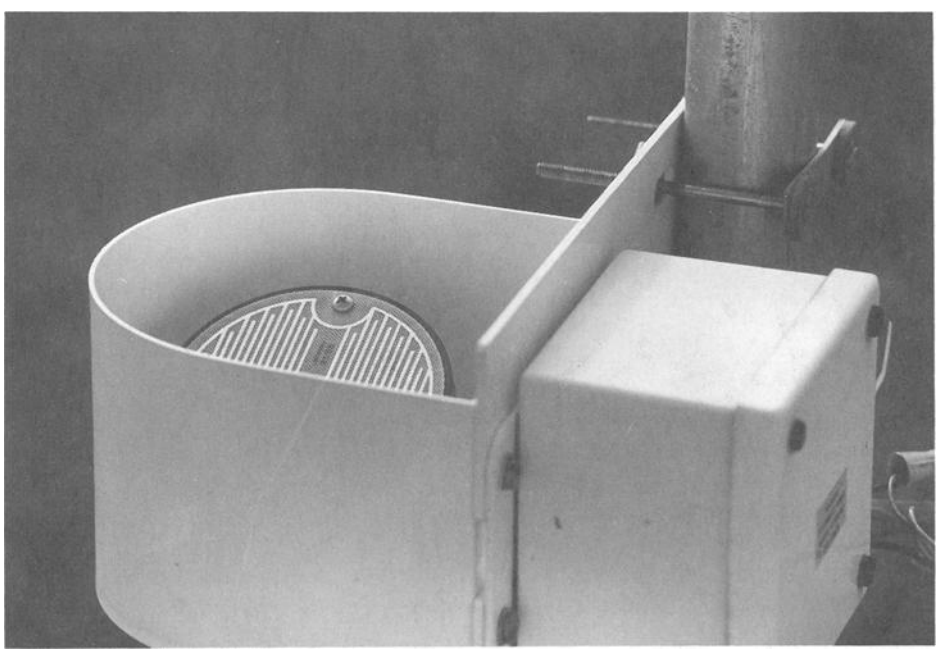

FIG. 24–Rainfall duration sensor.

ture of the sensor above the dew point will also prevent condensation from forming.

In addition to the specialized instruments detailed above, many more recognizable parameters must be measured. Ambient temperature and relative humidity can yield general information concerning the climate at the test site and the condition of the atmosphere surrounding the exposed specimen. These measurements are made following World Meteorological Organization (WMO) practices with mercury thermometers, psychrometers, or—more commonly—recording hygrothermographs in a WMO shelter (Fig. 25). Wind speed is a factor in the cooling of paint panels and is measured with an anemometer. A rain gage (Fig. 26) collects rainfall to determine the amount of precipitation. The rate of rainfall can be important; 25 mm in 30 min can be quite different from the effect of 5 mm in 2 h.

All of these data can be collected and displayed in such a manner as to characterize a weathering climate. If the influencing parameters are compared, it is possible to convey the severity of the weather with respect to the exposed materials (Fig. 27).

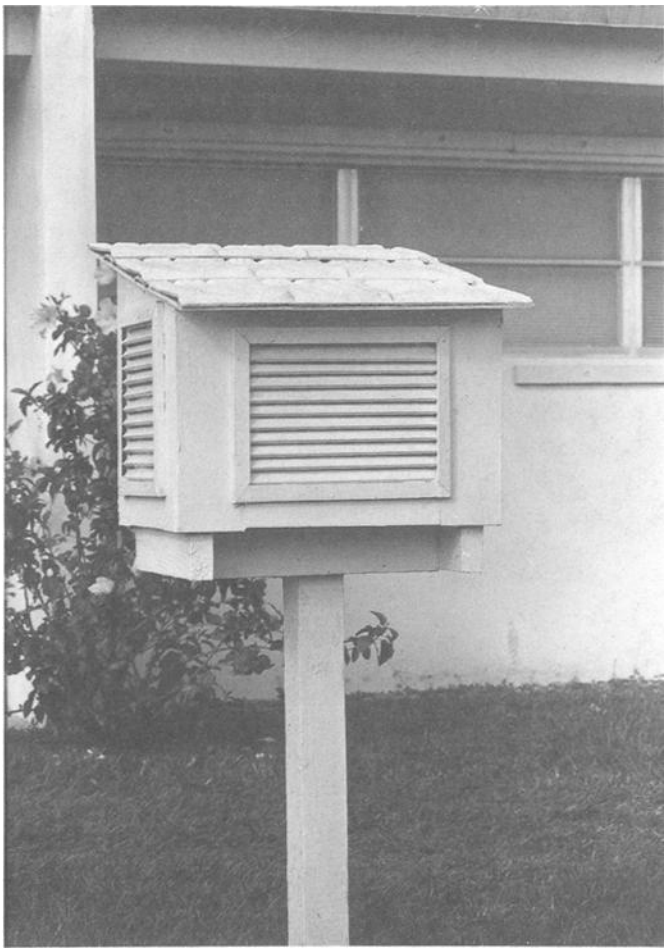

FIG. 25–WMO instrument house.

FIG. 26–Rain gage.

EXPOSURE TYPES

Exposure Frames

The most common type of exposure frame in use today is the aluminum rack designed for open (unbacked) exposures (Fig. 28). This type of rack and associated hardware should be constructed with noncorrodible material to prevent any contact corrosion effect with a specimen. Typical racks consist of a rectangular frame, adjustable hinged flaps with vinyl strips, and a clamping device to keep specimens securely fastened (Fig. 29). This type of exposure frame is very versatile in that it can be tilted to any specified angle or direction and can be adjusted to accommodate different-size specimens. Some advantages in using this type of frame are: (1) any size specimen can easily be mounted and removed, and (2) the hinged flap with vinyl strip can be adjusted to protect the top portion of the specimen so that any changes in appearance resulting from weathering can be detected.

Another type of exposure frame is known as the "black box" (Fig. 30). This insulated exposure is used mainly for recreating the conditions found on the flat surfaces of an automobile. It consists of an aluminum box painted black and open on top. Panels to be tested are placed over the open top side. If there are insufficient panels to cover the open area, black

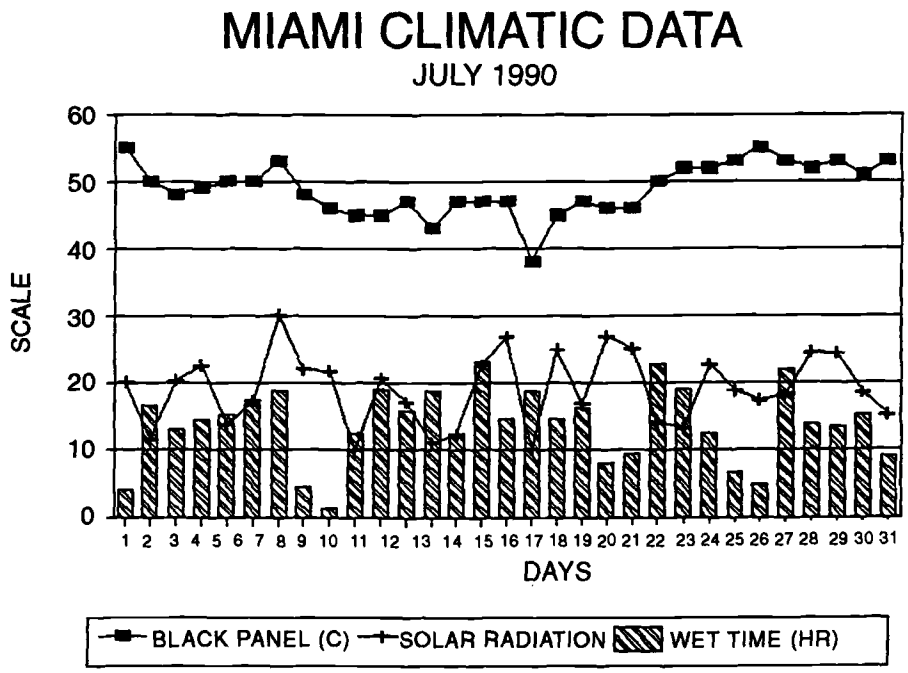

FIG. 27–Monthly weather summary, Miami, Florida.

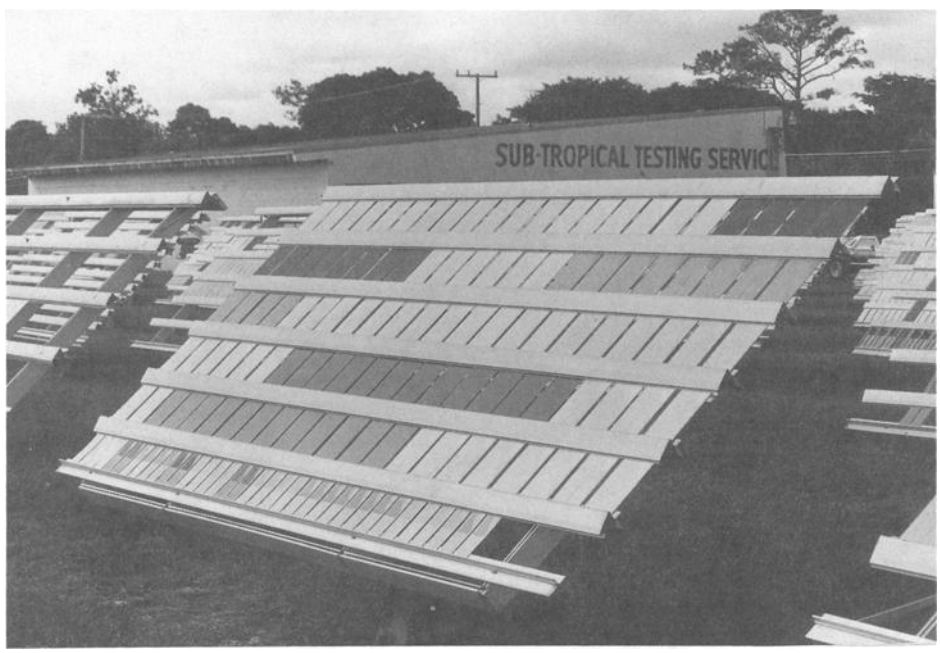

FIG. 28–Exposure rack with panels.

metal "dummy" panels must be used to completely cover the top side to maintain a high temperature during the daytime.

A third type of exposure frame in use but to a lesser degree is the solid wood rack. Like the black box, this frame also elevates sample temperature, but not to the degree of a black box. Generally, ¾-in. (19-mm) untreated plywood is used when constructing this type of rack. Depending on the condition to be simulated, the plywood can be left unpainted or painted black to further increase sample temperature. Using this type of frame is commonly referred to as "backed exposure."

Exposure Angles

The choice of exposure angle that a paint manufacturer uses for outdoor weathering is a critical decision. The angle of the specimens on exposure have a definite impact on the amount and type of degradation that can be generated. The exposure angle will affect the amount of solar radiation de-

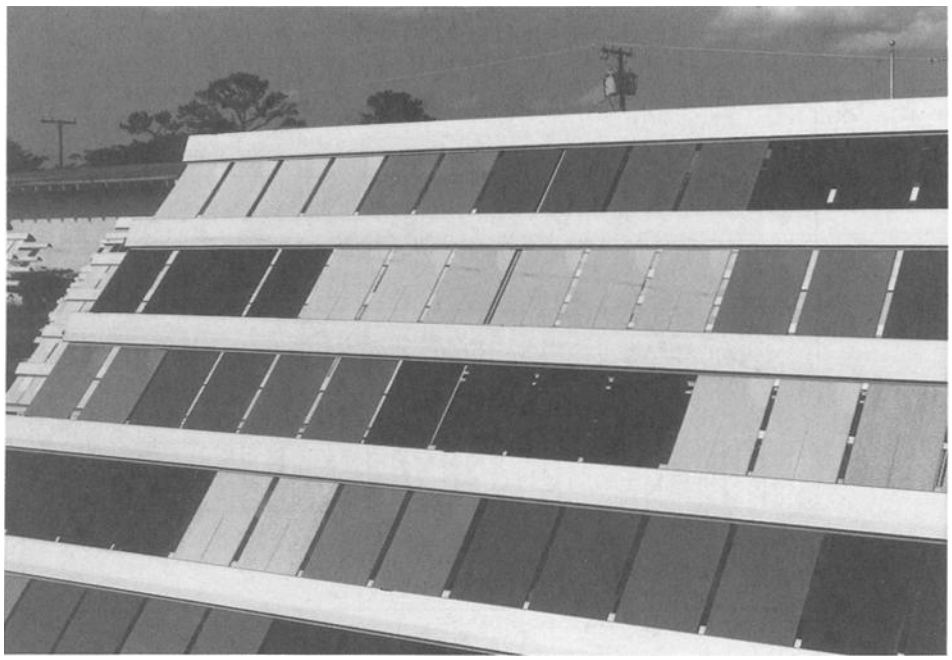

FIG. 29–Closeup of panels on exposure.

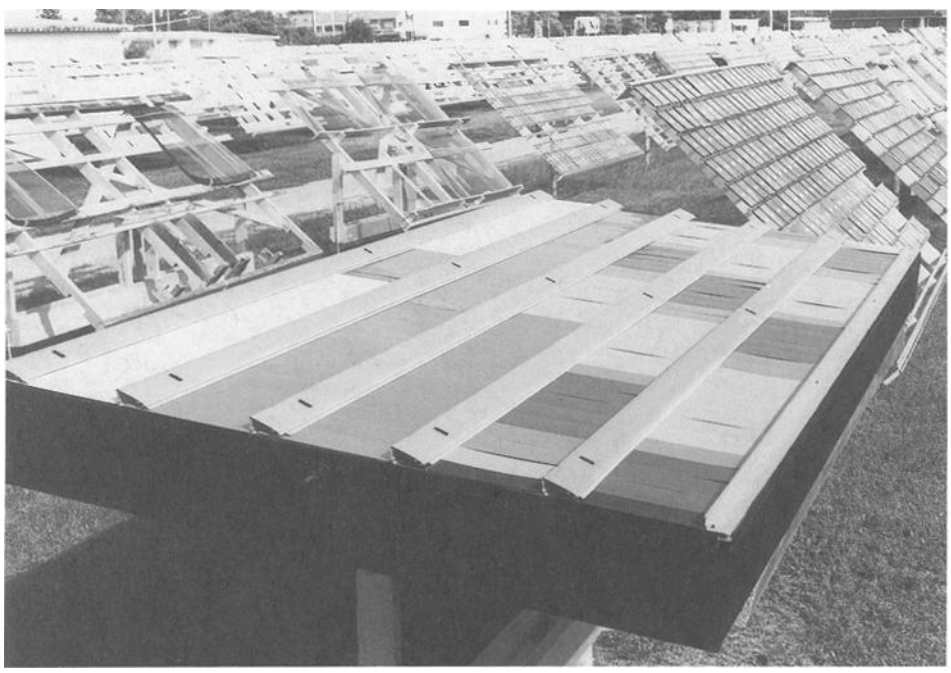

FIG. 30–Black box at 5° south.

posited on the sample, the amount of time the sample remains wet from rainfall or dew, and the temperature of the sample (Table 4). To generate meaningful test results, it is important to expose specimens at an angle similar to end use.

The basic angles of exposure that are used most commonly are as follows:

1. *45 Degrees South*—Specimens are exposed at an angle of 45° from horizontal and facing the equator (see Fig. 28). This is the most common angle used for architectural house paints and industrial coatings. This angle is also

TABLE 4—Panel exposure temperatures.

	Temperature, C			
	Maximum		Minimum	
Exposure Type	White	Black	White	Black
Open back, 45°	45	60	20	18
Solid back, 45°	50	70	19	17
Open back, 5°	48	67	20	18
Solid back, 5°	52	73	19	17
Black box, 5°	55	76	17	15
Ambient air	(32)		(20)	

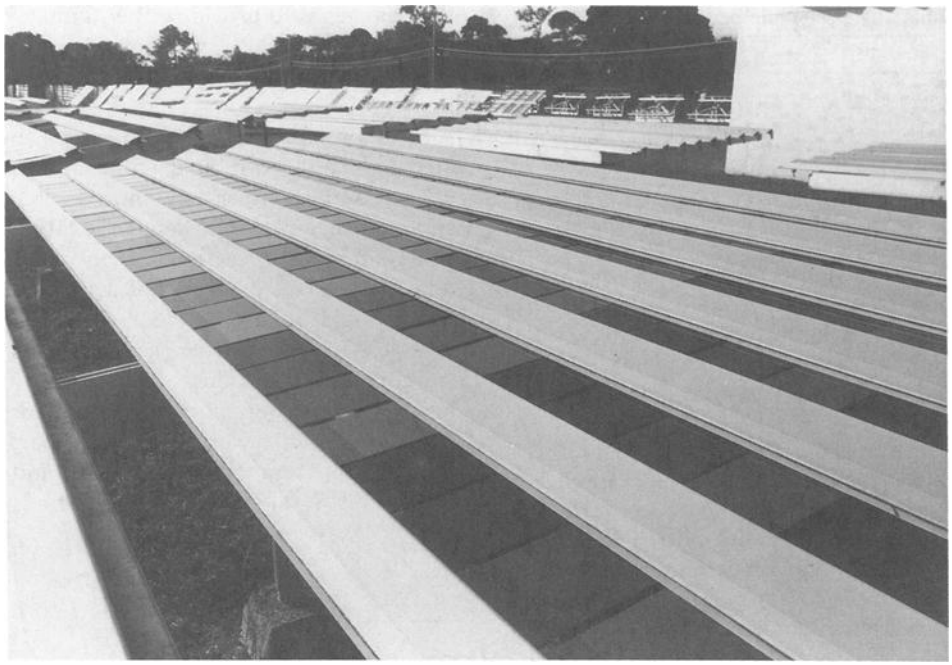

FIG. 31–Panels on exposure at 5°.

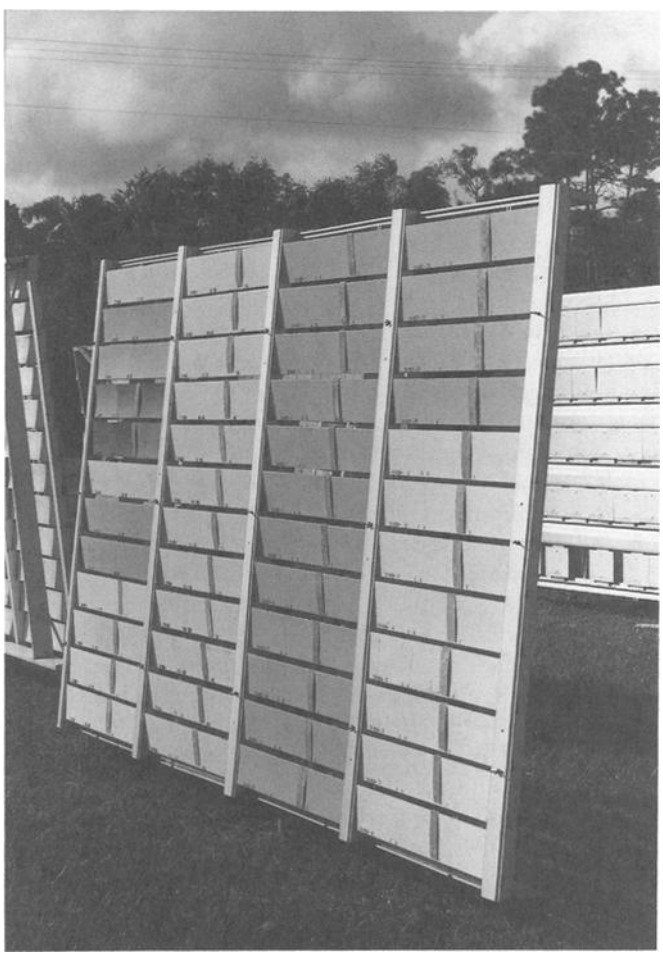

FIG. 32–Wood siding panels on exposure at 90°.

used as a compromise when end use position is unknown or variable.

2. *5 Degrees South*—Specimens are exposed at an angle of 5° from horizontal and facing the equator (Fig. 31). This angle is preferred over horizontal to avoid water ponding on the sample. When exposing in a subtropical environment, the 5° angle will increase the yearly amount of solar radiation, especially during the summer, and also the total time of wetness when compared to 45° south. This angle is also used for black box testing and for automotive finishes.
3. *90-Degree Racks*—Specimens are exposed at a right angle to the ground (Fig. 32). Exposure racks can be facing north or south depending on the end use of the coating. Generally, when testing for mildew resistance, architectural paints are exposed vertically (90°) north to maximize moisture retention.
4. *Station Latitude*—Exposure frames are tilted so that the specimens are exposed at an angle from horizontal equal to the geographic latitude of the exposure station. For the two benchmark weathering locations, Miami, Florida is at 26° latitude and Phoenix, Arizona is at 34° latitude.
5. *Variable Angle*—The angle of exposure of the specimens is changed on a seasonal basis to ensure maximum solar radiant exposure. For the Miami, Florida weathering location, the schedule calls for 5° exposure in the summer, 45° exposure in the winter, and 26° in the months of the equinox (see Table 5 for angle schedule).

Orientation

Standard exposure is for the specimen to face the equator. In the Northern Hemisphere this means that south is the predominant direction for the exposure of specimens. This is the most severe direction as it enables the sun to shine directly on the specimens for a greater portion of the day. Exposures in any other direction would only be used if any

TABLE 5—Variable angle schedule per ASTM E 782.

Month	Tilt Angle
March	Latitude angle
April–August	Latitude angle − 20°
September	Latitude angle
October–February	Latitude angle + 20°

NOTE: Latitude angle = tilt angle equal to the latitude at the exposure location.

other factor of influence was concentrated so heavily in a different direction that it took precedence over the solar influence. This may be the case where marine atmosphere exposures are used and the sample faces the shoreline rather than south.

The major exception to the south exposures is found with the testing of paints for residential use. Paint applied to wooden sidings is extremely susceptible to the effect of mildew attack, especially on the shaded side of the house, which is predominately more conducive to fungus growth. A vertical (90°) north exposure is common for painted wooden sidings. However, at times, equal mildew growth on replicate specimens has been observed by the author on vertical (90°) south exposures.

Mounting

There are several different methods for mounting specimens onto a test frame. The type of backing chosen depends more or less on the material being tested and the end use application. Generally, since most paints are applied to a wood, aluminum, or steel substrate, mounting of specimens is done on an open-backed rack. However, if a somewhat accelerated test is necessary or a specimen must be tested to a particular standard, then mounting specimens in a black box might be necessary. A different mounting technique would apply to residential siding material. In this case, mounting against a wooden backing would more closely simulate end use conditions.

Another important criterion that can have an effect on the outcome of an exposure test is the location and surrounding obstructions in the immediate area of the test site. In accordance with ASTM Practice for Atmospheric Environmental Exposure Testing of Nonmetallic Materials (G 7), the test rack is to be placed in a location so that no shadow from a neighboring obstruction shall fall on any specimen when the sun's angle of elevation is greater than 20°. Also according to ASTM G 7, the area beneath and in the vicinity of the weathering racks should be characterized by low reflectance and by ground cover typical of that climatological area. In desert areas this will be gravel, whereas in most temperate areas the ground cover will be low-cut grass.

ACCELERATED NATURAL WEATHERING

The possibility of deriving an accelerated test from outdoor exposure seems like a misnomer. There are, however, many test methods that aim to do just that. The basic idea is very simple: to artificially increase the severity of the outdoor exposure to boost degradation rates. The secondary aim of the changes is to provide either a more realistic exposure or to produce faster deterioration without the loss of any agreement in test results compared to the actual end use environment [*14*].

Outdoor exposure in Miami can be considered an accelerated test in its own right if the intended comparison is to exposure in a temperate or northern climate. All the necessary parameters are present in greater amounts. The corollary is simple: increase the severity of the influencing parameters and the rate or degree of deterioration will increase.

A straightforward outdoor test involves positioning the sample on a frame where the elements of the weather can work together to produce the deterioration. To accelerate the overall weathering process, one or more of the influencing parameters can be increased. The parameters that can be increased are temperature, wetness, and solar radiation, and there are several standard test methods designed to do just that.

Black Box

The first parameter normally modified when there is a need for acceleration is the test for specimen temperature because it is the easiest to control. There will be an increase in the rate of the forward degradation reaction as the thermal load is increased.

The simplest way to increase the temperature is to position the specimen on a solid backing of dark color with a high insulation factor (R). This method is widely used for residential sidings, roofing materials, and others. A comparison of the temperatures of black and white panels on various exposure frames on one summer day in Florida is shown in Table 4.

The black box exposure is used to test automotive finishes, and its specific purpose is to increase the temperature of the test panels to the same as the nearly horizontal surfaces of a car. This test method is described in ASTM Practice for Conducting Accelerated Outdoor Exposure Tests of Coatings (D 4141). Committee D01.27 on Accelerated Testing of Paints has conducted several studies regarding the black box [*17*], which was originally developed by General Motors. The box is made of aluminum, painted black, with the paint panels forming the top surface. The black box exposure also serves to lower the panel temperature overnight below that of the surrounding air, creating a longer condensation period.

The conditions as they affect the paint panels are a good simulation of the actual end use condition, so this test may be considered by some not as an accelerated test but as one that is realistic of the end use for that climate. If the definition of an accelerated outdoor test is one where the influencing conditions are altered over the open-backed direct weathering test, the Black Box Test is indeed an accelerated test.

A further acceleration is introduced using the Heated Black Box Test. This is a black box incorporating heating elements inside the air space. The air temperature inside the box is maintained at an artificially high level even when there is no incident solar energy.

Salt Spray

In Florida, corrosion tests are accentuated by spraying with salt water in the Scab Test. This uses the natural effects of the weather to break down the coating, then increases the corrosion at a scribe mark.

The paint panels are exposed to direct weathering at either 45 or 5° and are sprayed at regular intervals (normally twice weekly) with a 5% sodium chloride solution (Fig. 33). The spray is scheduled for times when the paint panel will be dry, thus maximizing the absorption effect.

This test has proven to be an excellent method for determining the corrosion resistance of automotive coatings. The advantage is that the results are very similar to the results of actual car corrosion determined from field studies. The simultaneous effect of sunlight and saltwater produces an overall deterioration effect rather than a single failure mode as is usually given by salt fog tests such as ASTM Test Method of Salt Spray (Fog) Testing (B 117).

Spray Rack

The stresses due to moisture vapor content into and out of the specimen are important for the overall breakdown of most materials. Moisture vapor acts as a catalyst in the photochemical breakdown process. In Arizona's desert environment with high temperature and solar radiation, exposure tests are accelerated using the spray rack, which wets the specimens on a regular basis during the day and overnight. The result produces an effect similar to Florida exposure, plus a slight speedup in the deterioration rate. This rate of increase has been seen as ranging from one to two times the rate for direct weathering in Florida.

The exposure is conducted as a solid-backed direct weathering, with the specimens sprayed daily on a regular basis during the night and/or day with distilled or deionized water. The day-time spray is normally of very short duration, intended as a harsh thermal and moisture shock to the paint surface. The nighttime spray cycles are of longer duration, intended to soak the paint thoroughly in a simulation of the overnight condensation effect. This occurs naturally very rarely in the desert of Arizona.

Both of these accelerated outdoor tests recognize the importance that wetness plays in deterioration. One important note here is that the timing of the water application is vital to produce the correct type of failure.

Follow the Sun

Increasing the level of solar radiation for an outdoor test can be done in two ways. The exposure frame can be designed to track the sun across the sky so that the specimens remain at normal incidence, which will yield greater radiant exposure. The limit for this test method is that the intensity level cannot exceed 1 Sun. A simpler method simply adjusts the tilt angle of the rack in response to the height of the sun in the sky. This "variable angle" exposure uses the schedule outlined in ASTM Practice for Exposure of Cover Materials for Solar Collectors to Natural Weathering Under Conditions Simulating Operational Mode (E 782), which is summarized in Table 5 and is based on the latitude of the exposure. The effect is to increase the solar radiation dosages up to 10% over the fixed latitude angle rack.

Fresnel Reflector Concentration

An equatorial mount using an array of mirrors to reflect sunlight back onto an exposure frame will greatly increase the incident solar enegy (Fig. 34). This is the Fresnel Reflector Concentrated Sunlight device, as specified in ASTM Practice for Performing Accelerated Outdoor Weathering of Nonme-

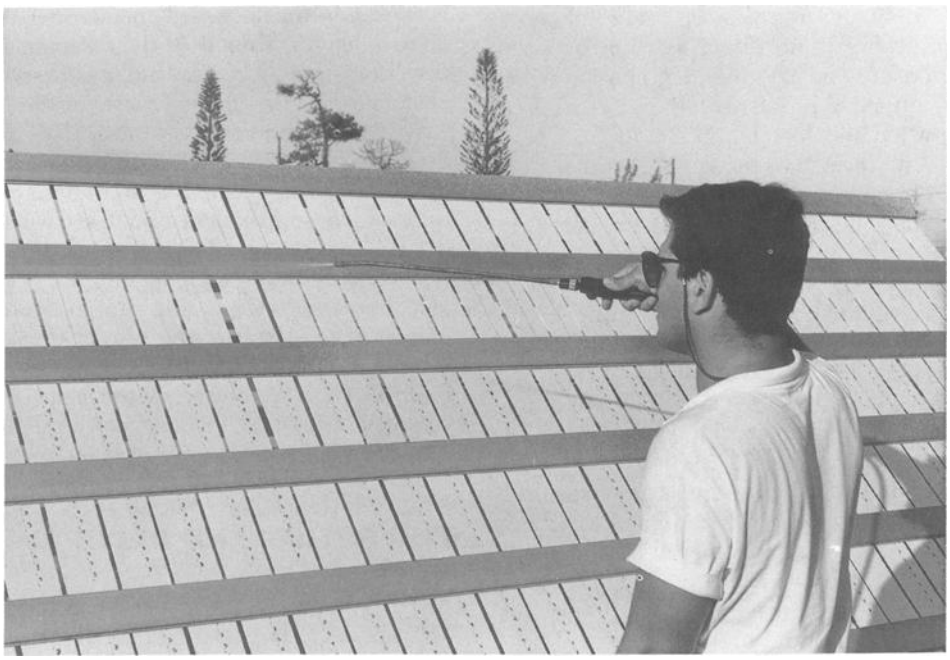

FIG. 33–Salt spray testing (Scab Test) in Florida.

FIG. 34—Fresnel reflector concentration device.

tallic Materials Using Concentrated Natural Sunlight (G 90) and when used for testing coatings per ASTM D 4141. This type of exposure is more closely related to that produced by another accelerated device, the xenon arc, than to outdoor test methods. The concentration is a factor of one for each mirror (less the efficiency of the reflector, which is about 80%), so in effect the solar irradiance on the specimen is about eight times the normal incidence tracking frame. The high intensity of the light exposure causes the sample temperature to rise also; if a water spray cycle is added, all weathering factors are increased.

The high intensity of the solar energy on the paint causes deterioration rates of 4 to 16 times the rate for non-accelerated exposure. There is no direct relation between amount of radiant exposure and extent of degradation when the irradiance level is altered. Caution must therefore be used when quoting acceleration and correlation factors from testing on this machine. With the sun as the energy source, most of the problem of matching light sources is removed. This can occur when using some laboratory-accelerated weathering devices.

The paint panels are mounted on a target board that is positioned upside down on the bottom of the air tunnel. The mirrors are arranged in a Fresnel array, whose focal point is the target board. The panels are cooled by forced air from the air tunnel, which is directed across the front and back of the panel. A set of nozzles is positioned so that water spray may be directed onto the face of the panels.

The device works optimally when there is unobstructed direct beam radiation as the machine is designed to follow the sun and reflects only the incoming energy from a small solid angle. It is important, therefore, for the machine to be aligned with the sun at all times during the day. Clouds will disrupt the optimum condition, and overcast days will prevent the Fresnel Concentrator from operating at its most efficient. As a result, the machine is normally employed in the desert, where clear skies and strong sunlight are found almost every day. It would be incorrect, however, to say that this device will not work correctly out of the desert environment; the time for accumulation of energy, however, would be greater.

The test duration for the Fresnel Concentration is determined by solar radiant exposure, normally the total ultraviolet. As the energy levels at the target board are too high for direct measurements on a permanent basis, the dosage must be calculated from direct measurements using a correction factor for the reflectance of the mirrors. The mirror material is chosen for its flat reflectance properties, thereby reflecting all wavelengths equally. If the reflectance value of the mirror material is monitored closely, it is possible to make accurate calculation of the intensity level at the specimen position.

When the irradiance is integrated, dosage levels for the Fresnel Concentration Device are eight times greater than normal incidence. One year of radiant exposure from a fixed rack can be reached in about six weeks exposure on this device.

The common thread to all outdoor accelerated (or accelerated outdoor) tests is that one or more factors have been increased to speed up the rate of the deterioration. This is usually intended to give the test a more realistic comparison to an intended end-use environment. The exception to this would be tests that increase solar intensity above naturally found levels.

INSPECTION AND REPORTING

Visual

Interim inspections of a material to chart the degradation progression throughout an exposure period will produce im-

portant information on the rate at which a sample degrades and at what time interval certain properties become noticeable. To accomplish this, visual or instrumental techniques are used to assess the severity of degradation.

When visual inspections are performed at periodic intervals, a number of variables are introduced that make it difficult to get consistent and repeatable assessments. To minimize these variables, inspection procedures must be standardized. When viewing specimens for color change or for weathering effects, it is very important to use the same light source and viewing conditions. For this reason, evaluations are conducted according to ASTM Practice for Visual Evaluation of Color Differences of Opaque Materials (D 1729). In this test method, spectral qualities are outlined for different light sources, which are to be used for various evaluations. A viewing booth will allow the most consistent readings over an extended period of time as opposed to examining changes outdoors where daylight is not always the same.

Reporting Scales

When evaluating the ability of a coating to withstand weathering effects, the changes over a period of time must be charted. To do this with consistency, reporting scales are employed to record the amount of change. In many instances it is not practical for the person most interested in the durability of a coating to see how a particular coating performs over a period of time. This is quite often the case as specimens are exposed in a different country or region of the United States in order to achieve answers in a shorter period of time. This makes it necessary to leave the inspection process up to another individual. A problem is the fact that no two people perceive a degree of change in exactly the same way. In order to minimize this problem, certain procedures are followed so that all interested parties will "see" the defect(s) the same way. This is done by using generally accepted examination procedures and the use of photographic reference standards.

The American Society for Testing and Materials (ASTM), the Federation of Societies for Coatings Technology (FSCT), and the International Standards Organization (ISO) each have examination procedures similar in quantitative descriptions. The main difference lies in the quantitative and qualitative numbering scales used. FSCT uses a scale from 10 to 0, with 10 being "perfect" or "absent of failures." ISO uses a scale from 0 to 10, with 0 representing an "unchanged" condition. Independent test labs in the United States use the ASTM/FSCT scale in their ratings unless instructed otherwise by their client. It should be noted that "perfect" is not a preferred term, and the testing labs will use the term "as received."

Failure Modes

Evaluating and recording type and degree of failure modes in a particular coating is not a difficult task if visual inspections are performed properly. Although most ratings are subjective in terms of degree of failure, an experienced and well-trained inspector consistent in his or her ratings is able to portray a good image of any degradation present. In order to do this, all relevant standards including the FSCT pictorial standards must be used when applicable. Table 6 lists the more commonly used evaluation standards for paint failure reporting. More complete descriptions of these effects can be found in other chapters of this manual.

TABLE 6—List of surface appearance standards.

Property	ASTM Method
Color change (v)	ASTM D 1729
Chalking	
Manual	ASTM D 4214
Tape	ASTM D 4214, TNO
Dirt retention (p)	
Mildew growth (p)	ASTM D 3274
Checking (p)	ASTM D 660
Cracking (p)	ASTM D 661
Flaking (p)	ASTM D 772
Blistering (p)	ASTM D 714
Surface rust (p)	ASTM D 610
Scribe rust (p)	ASTM D 1654
Erosion (p)	ASTM D 662
Color (i)	ASTM D 2244
Gloss (i)	ASTM D 523
D of I (i)	ASTM E 413

NOTE: (v) = visual; (i) = instrumental; (p) = pictorial.

Nondestructive

Nondestructive testing is aimed at inspection without the disturbance of the integrity of the specimen. This will, by the above definition, include mostly all the visual evaluations and all the instrumentally assisted optical measurements. True nondestructive testing, however, is aimed at investigating defects that cannot be seen easily with the eyes or surface scanning equipment.

Nondestructive tests aim to determine physical changes in the structure of a material that cannot be determined visually. It is particularly useful in seeing changes at the molecular level, in the bulk part of the material, or in underlying layers.

Many of the common physical tests employed to assist in evaluating the effect of weathering are in fact "destructive." The paint sample is disturbed during the measurement process, as in testing adhesion or chalking. When a destructive test is used, several disadvantages are evident: the specimen cannot continue exposure because the place where the test was conducted will affect the continuity, and a permanent record of the condition at that time is lost. These problems can be overcome by using a large number of replicates so that there will be enough virgin material for testing.

When the same sample can be studied throughout the test, it may be easier to get a much clearer picture of the sequence of events of the progression of failure mechanism. This is especially true at the earliest sign of changes in the material. If it is possible to determine the changes that occur at the molecular level during the initial stages of deterioration and follow the progression through to failure, it is possible to develop models which will assist in predicting long-term durability from short-term testing.

The range of methods included in nondestructive testing is varied, and Table 7 lists those which have been demonstrated to have an application in weathering.

TABLE 7—List of nondestructive testing methods.

Property	ASTM Method
Electromagnetic	ASTM D 1186
Strain gage	...[a]
Infrared thermography	...[a]
Electron microscopy	...[a]
X-ray radiography	...[a]
Ultrasonic holography	...[a]
Video imaging systems	...[a]

[a]Standard for application to coatings being developed.

TABLE 8—List of physical testing standards.

Property	ASTM Method
Impact	ASTM D 2704
Elasticity	
Elongation	ASTM D 522
Bend	ASTM D 522
Hardness	ASTM D 3363
Adhesion	ASTM D 3359
Abrasion	ASTM D 4060
Mar	
Chip resistance	ASTM D 3170

Mechanical Properties

There is a major distinction that must be made between surface appearance changes in a material and intrinsic physical properties. Changes can occur on the surface without affecting the bulk of the material.

A major portion of a complete weathering program is the measurement of the physical changes produced during exposure. A result of UV degradation and associated failure modes can have a direct impact on the relationship between stress and strain of a coating and the elastic and inelastic reaction when force is applied. To have a better understanding of the true performance of a weathered specimen, it is necessary to perform tests to determine certain mechanical properties. Table 8 lists the more commonly performed mechanical tests on weathered paint panels. A more complete description of their relevance is given in other chapters of this manual.

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Accelerated Weathering

by Valerie D. Sherbondy[1]

PAINTS AND COATINGS ARE USED both to protect substrates and to provide an aesthetically pleasing appearance. In an outdoor environment, both of these functions can be affected by weathering. The four major factors involved in weathering are sunlight, moisture, oxygen, and heat. Light, especially in the ultraviolet (UV) region, may lead to discoloration, premature loss of gloss, scaling, embrittlement, and chalking. Moisture may cause blistering, flaking, mildew, and early loss of adhesion. Heat may cause embrittlement, cracking, peeling, and checking. Oxygen in the atmosphere promotes oxidation of the surface of the coating, which may eventually lead to oxidation of internal layers, causing embrittlement, softening, cracking, or crazing. These elements contribute individually as well as in combination to cause coating failures.

Naturally occurring and man-made chemicals in the environment also contribute to coating degradation and could be considered a fifth element of weathering. However, the type and levels of chemicals can vary dramatically, even over short distances. Therefore, they cannot be considered as universal in character as the four factors mentioned previously. Perhaps as a consequence of this, and also partly due to tradition, chemical resistance testing is usually considered to be separate from artificial weathering. Therefore, this chapter will consider only those devices that incorporate an ultraviolet light source. Although the effects of chemicals cannot be ignored, they are discussed elsewhere in the manual.

Accelerated or artificial weathering involves the use of laboratory equipment to simulate the degradation that occurs during actual outdoor exposure [*1–3*]. Accelerated weathering is the term most often applied to artificial weathering because the elements of light, heat, and moisture are either longer in duration or more intense than the actual time and conditions encountered in outdoor exposure. This causes the coating to weather or degrade more rapidly, in a time sense, than when placed in a natural environment. However, in an attempt to accelerate the effects of natural weathering, the laboratory conditions may be overly aggressive and thus cause results that are not attained during natural weathering.

Artificial weathering devices should be designed to produce test conditions that are controllable and reproducible, so that data are reproducible on a day-to-day basis and comparable on a laboratory-to-laboratory basis. This differs from outdoor or natural weathering where there are no controls over environmental factors. Due to this variability of conditions, the results of natural weathering often are not reproducible. For example, weathering factors are different for various parts of the world and for different countries. Some locations receive more sunlight and heat, while others are cloudy and cool. There are also seasonal variations. Even for long-term testing, the data for a specimen placed outside during January would not necessarily concur with data for a duplicate specimen placed outside in July because of initial exposure effects. Even if the same location and time of year are used, the natural weathering factors change from year to year. In contrast to natural weathering, data produced under controlled laboratory conditions can be used as comparative data, assuming the same equipment, equally aged lamps, etc., even if testing was conducted during different times of the year or over several years.

In addition to reproducibility, a great advantage of accelerated weathering is that the results are available more quickly than with natural weathering, which is a phenomenon that may take years. The time saved on testing can translate into cost savings when developing new products or when choosing a new coating system for buildings, tanks, or equipment where historic data about coating performance are not available.

Even though there are many advantages to accelerated weathering, it is important to recognize that these data should be used for comparative purposes only since at this time a direct correlation to natural weathering has not been proven for any weathering device currently being used. One reason a correlation has not been developed is because data obtained through artificial weathering have been produced by subjecting the sample to unnatural conditions, and the results may or may not duplicate those found during natural weathering. If similar failure modes are experienced in an accelerated weathering device and at an outdoor test site, a direct correlation may be developed for that product. The calculated correlation would be valid only for the tested material under the stated, specific conditions, and the actual field conditions usually differ from the conditions found in a test fence area.

It should be noted that not all results obtained by accelerated weathering devices are reproducible [*3*]. Studies have concluded that even though the settings may be the same, the maintenance of the device—including light source, filters, and gauges—affect the exposure levels and thus the results of the testing. The cleaning and disposal of light filters is often subjective and a major source of variation that changes the amount of light at critical wavelengths. The intensity of the light is also dependent on the changing of, rotation of, and power supplied to the light source. These factors may speed

[1]Assistant laboratory director, KTA-Tator, Inc., 115 Technology Drive, Pittsburgh, PA 15275.

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up or slow down the degradation process due to changes in both temperature and UV light exposure. Since this is known to occur, testing specifications are sometimes written to include a standard material with the test specimens or to include an actual measurement of the light during the testing. This measurement is discussed later in this chapter.

Even if the light source was not changing with time, each device has areas of more intense exposure. For this reason, most devices have recommended manual rotation procedures for the exposed specimens. These procedures should be performed at regularly spaced intervals to decrease the effects of uneven exposure. These effects would be greater on short-term tests, where the specimens would not be moved through the different stages.

Aside from the conditions of the device, the conditions surrounding the device also affect performance. Most devices require a ventilated area to maintain ambient conditions so temperature changes within the device can be maintained or obtained. For example, a relatively high ambient temperature may reduce the amount of condensation on some devices, while high amounts of ventilation may slow the temperature recovery after a water spray in other devices. It should be noted that ambient conditions are not specified by ASTM standards, although the manufacturers recommend general guidelines. Ambient conditions will vary between laboratories, adding an unknown variable that may affect the results.

ELEMENTS OF WEATHERING

There are many component factors that contribute to the weathering of a coating. The general components are light, moisture, heat, and oxygen, which are always present in various amounts. This section concentrates on these general components and on how they are simulated and intensified.

Light [4]

Sunlight is composed of light from the visible, ultraviolet, and infrared regions of the electromagnetic spectrum (Fig. 1). The damaging region of sunlight has been determined to be the ultraviolet light (UV) region, especially the shorter wavelengths ranging down to 295 nm. The portion of sunlight in the UV region is relatively small, only 5 to 7%, due to the filtering effects of the atmosphere. The UV region has been divided into three domains: UV-A, UV-B, and UV-C. The UV-A region is 315 to 400 nm, the UV-B region is 280 to 315 nm, and the UV-C region is 200 to 280 nm. Although the UV-C is the most damaging region, these wavelengths are filtered out by the atmosphere. Therefore, if light sources produced output in this region, they would cause abnormal degradation and their use should be avoided when performing accelerated weathering unless there is a possibility of UV-C exposure.

Both the UV-A and the UV-B regions cause degradation of coatings. The energy of the shorter wavelengths present in the UV-B region, ~91 to 102 kcal/mol (3.8 to 4.3 J/mol), cause more severe and rapid degradation of coatings than the wavelengths in the UV-A region. In the UV-B region, the energy levels are high enough to break carbon-nitrogen, carbon-carbon, nitrogen-hydrogen, carbon-oxygen, and carbon-hydrogen bonds in the polymeric portion of the coating. In the UV-A region, the longer wavelengths do not have sufficient energy, ~71 to 91 kcal/mol (3.0 to 3.8 J/mol), to break certain bonds, namely carbon-hydrogen. Thus, it is apparent that UV-A radiation differs from UV-B radiation in both wavelength and severity of damage.

The breaking of chemical bonds first leads to a degradation of the coating surface layers and is manifested by chalking, fading, and loss of gloss. Once the outer layers of polymer are lost, pigments are exposed. Without the protective polymeric binder, the pigments can fade and erode, causing a change in color and/or appearance.

Light has been simulated in accelerated weathering devices by mercury arcs, open and enclosed carbon arcs, fluorescent lamps, and reflection of collected sunlight. However, as the results produced by accelerated testing were compared to the results obtained from natural weathering, the light sources were modified to attempt to achieve similar results. Depending on the exact coating type and the service environment, several different specifications have been developed that indicate which light source should be used. Most of these test specifications require the use of open or "sunshine" carbon arcs, xenon arcs, and fluorescent lamps. These light sources were chosen since they were found to more closely simulate the degrading ultraviolet light range of sunlight or to rapidly produce dramatic changes in the coating.

Enclosed Carbon Arc

Originally, these lamps were used to test the light fastness of textiles. They were then combined with a water spray to be an industry-wide artificial testing device. Although mercury and carbon arcs have been in use for over 75 years, when they were used to test paint, it was discovered that they produce light that accelerates chalking and fading more than crack-

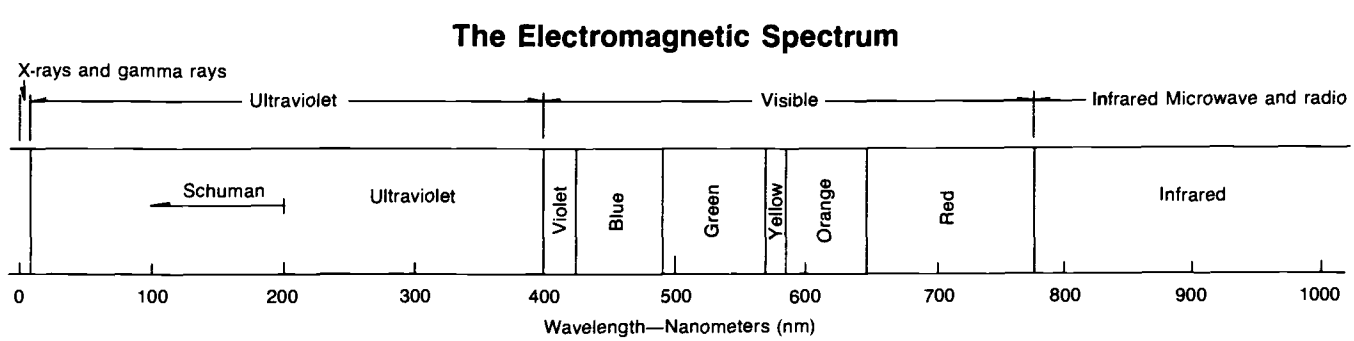

FIG. 1–The electromagnetic spectrum.

ing. The carbon arc consists of neutral solid and cored carbon electrodes. The flame portion of the lamp is enclosed in a borosilicate globe. The globe creates a semisealed atmosphere that sustains the arc and filters out UV light below 275 nm. The lamps produce two large spectral peaks that center near 350 and 380 nm, but they deliver essentially no emission below 340 nm, where the light is more severe in its degradation capabilities and more damaging to polymeric materials (Fig. 2). In addition, even the light in the visible region, 400 to 800 nm, was also low compared to sunlight, meaning that any visible color change due to the change of the pigment would require a lengthy exposure. As a result, the industry demanded a light source that provided a better simulation of natural sunlight, especially since more durable materials were being developed.

Open-Flame Carbon Arc

In response to industry demands, the open flame carbon arc or sunshine carbon arc was developed. This descendent of the carbon arc produced a spectrum closer to that of sunlight. The lamp operates in a free flow of air instead of in a globe. The lamp is composed of copper-coated electrodes and a central core of rare earth. The lamp is surrounded by a stainless-steel filter frame that also acts as an air duct. The frame holds flat, optical, heat-resistant, borosilicate glass panels that filter portions of the lower wavelength light from the spectrum. The spectrum produced by this light source is more similar to that of sunlight in the region between 310 and 370 nm (Fig. 3). However, there was still a spectral imbalance due to a large band between 370 and 450 nm, but the region between 450 and 800 nm was much closer to natural sunlight than the enclosed carbon arc lamp shown in Fig. 3. The disadvantage of this light source is the emission between 260 and 310 nm, which includes a portion of the undesirable UV-C region. Although this light source was an improvement, the industry requested the spectral distribution of the light be even closer to that of sunlight.

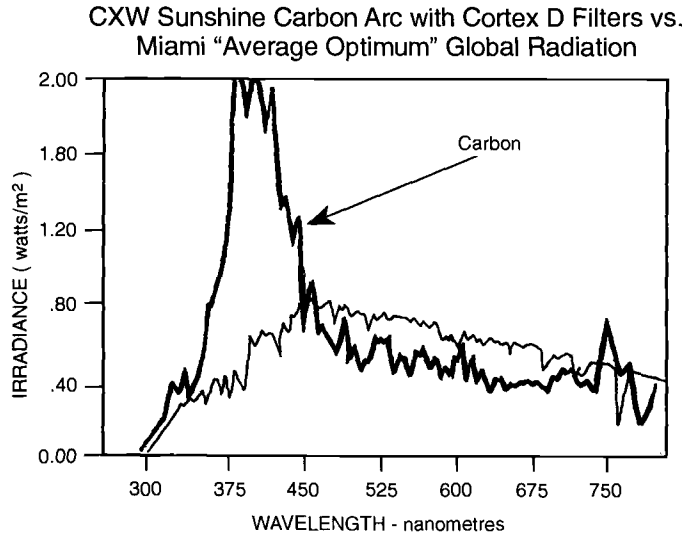

FIG. 3–Spectrum of light produced by a sunshine carbon arc. Used with permission of the Atlas Electric Devices Co.

Xenon Arc

The adoption of the xenon arc lamp for accelerated weathering devices was the next improvement in artificial weathering equipment. The xenon lamp consists of a burner tube and a light filter system. There are two types of xenon arc lamps. One type of xenon arc lamp is cooled by water circulated through the lamp housing. The cooling water also filters out the long-wavelength infrared light. The other type of xenon lamp is air cooled. Both lamp types produce a spectrum closer to sunlight when filtered and set at the correct irradiance setting. There are several filters and combinations of filters that can be used. The three common filter combinations used for artificial weathering of paint are quartz/borosilicate, borosilicate/borosilicate, and quartz/quartz. The first combination allows the UV region to extend down to 270 nm (Fig. 4). The borosilicate/borosilicate combination has a cutoff at 280 nm, which makes the spectrum closer to that of

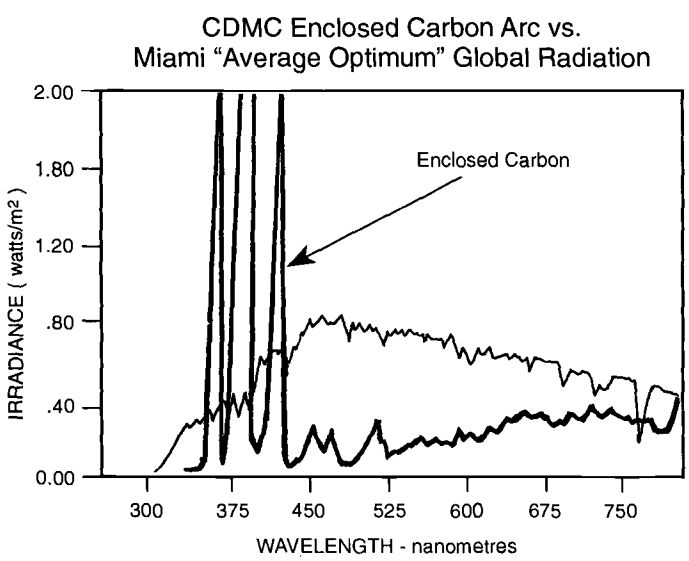

FIG. 2–Spectrum of light produced by an enclosed carbon arc. Used with permission of the Atlas Electric Devices Co.

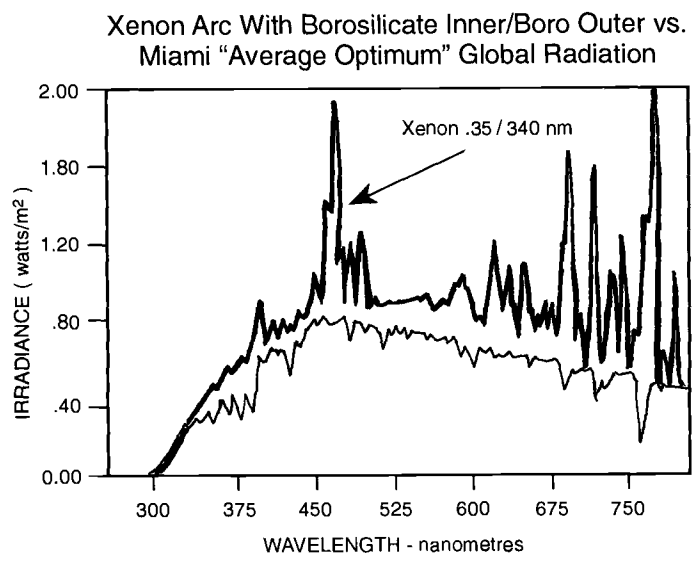

FIG. 4–Spectrum of light produced by a xenon arc. Used with permission of the Atlas Electric Devices Co.

natural sunlight, which cuts off at 295 nm. The quartz/quartz combination produces a spectrum that extends to below 250 nm, i.e., into the undesirable UV-C region, and although used to test coatings, it is the least popular of the three filter combinations.

Since the xenon arc source decays as the lamp ages, the irradiance of the light source should be monitored and can be controlled by adjusting the lamp wattage. Most new devices have a monitoring system to compensate for the decay. The most common settings are 0.35 or 0.55 W/m^2 at 340 nm. Both settings produce a spectrum with approximately the same cutoff wavelength (determined by the filter). The settings are both within the range of natural sunlight. The 0.55 W/m^2 setting is closer to summer sunlight, while the 0.35 W/m^2 setting is closer to winter sunlight. If the wattage settings are varied, the degradation rate will change.

Fluorescent UV Lamps [5,6]

The most recent development in light sources is the fluorescent UV lamp. These lamps were not developed to simulate the entire spectral range of natural sunlight. Rather, they simulate only the damaging UV region found in sunlight. Currently there are three types of fluorescent UV bulbs. The FS-40 and UVB-313 produce light with a maximum output at 313 nm (Fig. 5). The UVB-313 has a higher intensity and thus a greater weathering acceleration rate than the FS-40. The UVB-313 also has a higher, more stable output than the FS-40. Both of these lamps have outputs down to 275 nm, which is below the cutoff of natural sunlight. The third type of fluorescent lamp is the UVA-340 lamp that produces a spectrum very similar to that of natural sunlight (Fig. 6). The spectrum is made up of wavelengths in the UV-A region with a small amount of the UV-B region wavelengths. The cutoff matches that of natural sunlight. Although the results produced by the UVA-340 lamp are closer to that of sunlight, the UVB lamp is the most widely used fluorescent light source

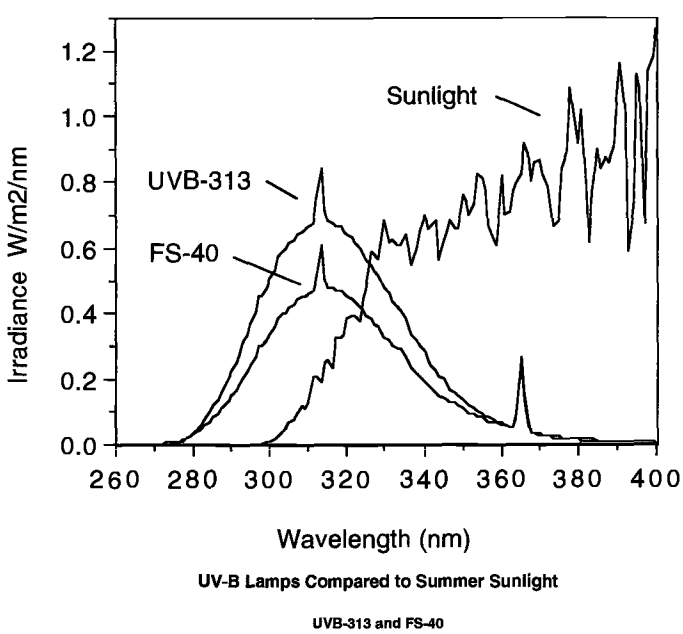

FIG. 5–UV-B lamps versus summer sunlight. Used with permission of the Q-panel Co.

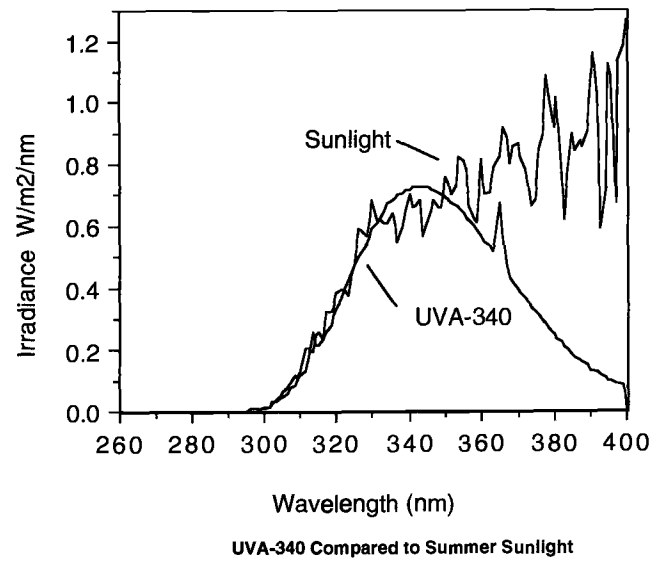

FIG. 6–UV-A 340 lamps versus summer sunlight. Used with permission of the Q-panel Co.

because of the rate at which degradation takes place. Since the cutoff of the UVA-340 lamp is higher, the degradation process takes a longer period of time than with the UVB-313 lamp, but may more closely match the degradation seen in the field. Both lamps are commonly used in the paint industry, and the choice of UVA or UVB lamp depends on the need for either speed or accuracy.

Lamp Stability

Once a light source has been selected, it is assumed that several tests run over a period of months or years can be used to evaluate the relative performance of the paints. However, this assumption is not always true. The xenon-arc source is currently the only device that always is sold with the irradiance measurement as an operating parameter and not just as an option. Even with this control, the output of the light source may vary depending on the care and maintenance of the device. The devices should be cleaned and changed as recommended to ensure the most reproducible and even spectral distribution and irradiance. The newer devices have the option of monitoring and adjusting the light output for all of the different light sources. In the future, these settings may become a required part of the report for the testing results.

There are several monitoring instruments available to measure the light output including pyranometers, radiometers, spectroradiometer, and light-sensitive materials. However, each of these devices may be used to measure different characteristics of light. Two different-colored light sources could produce the same response if a pyranometer is used to measure the light. These devices measure the amount of radiant power regardless of the spectral distribution. Even when filtered to restrict the wavelength of light being measured, it was found that the response was not sufficiently sensitive for the UV range.

Radiometers have been modified with filters to select areas of the spectral distribution. These are classified as wide band, broad band, or narrow band. The wide-band instruments

measure the light output over a range of several hundred nanometers. Broad-band instruments function over a range of 20 to 100 nm, while narrow-band instruments measure less than 20 nm. The most commercially successful radiometer measured the total ultraviolet light using a wide-band UV filter. However, when these devices were used to measure natural sunlight in comparison to the light sources, it was found that sensitivity to shorter wavelength UV was less than its peak sensitivity to visible light, which could be affected by temperature changes.

The currently used radiometer, developed for exterior monitoring, has a narrow band filter and a thermoelectrically cooled detector. This is suited for long-term use and is easily operated in the field by relatively inexperienced personnel.

For internal use and for the most accurate measurements, spectroradiometers are available. These would not withstand external use and normally require operation by skilled personnel.

In contrast to actual light measurements, there are industries, other than the paint industry, that rely on the use of light-sensitive reference materials. The reference material is placed on the cabinet at the same time as the test samples and monitored, usually for color changes, to evaluate the effectiveness of the light source. These materials must be inherently unstable to achieve the desired result. This instability should be considered when choosing a reference material. The reaction of some materials may vary widely, and the sensitivity is often a result of the total environment, so all of the other factors of exposure must remain constant. One of the major problems with using this technique in the paint industry is the short life of these materials relative to the more durable paint systems.

Even with all of the variability of light sources, proper care of the instrument can yield consistent results between laboratories. Most of these instruments have been run for many years with less monitoring and fewer quality-control procedures than are in use today, and the data have been acceptable over many years. This is due to the fact that most companies understand that the test results can only be used relative to other test results and to that end often include several competitive materials in the test protocol.

Moisture

Another important characteristic of weathering is moisture. Moisture is commonly overlooked as a significant factor of paint degradation because it is a common belief that structures are only wet when it rains, when they are splashed, and when they are immersed in fluids. Actual time-of-wetness studies have shown that samples placed outside in several different locations in the United States and Canada were wet approximately 30% of the time [7]. This averages to approximately 8 h per day. The water in a natural environment is caused by dew or condensation, rain, or melting snow or ice. The water may be absorbed or pass through the coating. If the liquid passes through and interacts or reacts with a water-soluble material, an osmotic cell may be formed. If it passes through the coating and reacts with the substrate, for example wood, the interfacial bond between coating and substrate may be destroyed or weakened.

The theory behind cyclic moisture exposure is based on the permeation of the test liquid into the coating, which may cause certain coatings to swell. During the drying cycle, reverse permeation or evaporation will occur, causing the coating to shrink, resulting in cyclic stressing of the system. The process by which degradation takes place and how fast it will occur is influenced by the permeability of the coating and the contact time required to initiate water penetration. The rate of water and chemical degradation is increased by increased temperature and ultraviolet light.

Moisture can be simulated by water spray, condensation, fog, or immersion. Depending on the device used, degradation acceleration is possible by increasing the number of wet/dry cycles or increasing the time of exposure. Since accelerated weathering devices run around the clock (and day after day for that matter), it is possible to cycle the specimen through several wet and dry periods and still meet or exceed the 8 h of average wetness found in natural weathering. Another way to accelerate the damage caused by moisture is to increase the time period of exposure to moisture. Prolonged exposure may degrade coating just as much as the stresses caused by wet/dry cycling.

Temperature

The third factor of weathering is heat or temperature. The degradation of coatings occurs more rapidly at elevated temperatures, and temperature variation can lead to expansion and contraction stresses in the coating. These stresses may be magnified by the expansion and contraction of the substrate itself, which can lead to cracking, peeling, checking, or loss of adhesion. Temperature can also accelerate the effects of other weathering factors such as light and moisture. In accelerated weathering, cyclic testing at only slightly elevated temperatures can produce accelerated results. The temperature chosen for testing should be within the expected temperature range of the service environment. Drastic increases in temperature are not necessary to produce noticeable effects and in fact should be avoided. Testing at excessive temperatures can either cause premature or unreasonable failures or even enhanced performance that would not be realized under actual use conditions. High temperatures may cause the coating to bake or cure excessively and cause it to become brittle with decreased impact resistance, or it may become more resistant to the environment than would occur if it were only air dried under ambient conditions. To prevent these occurrences, temperatures near those of actual or expected exposure should be used. The temperature should be monitored so the data have meaning relative to other test results.

Oxygen

Changing the degree of oxygen exposure of specimens by introduction of ozone or pure oxygen is possible with a few testing devices, but this modification technique is not commonly practiced. Oxygen exposure is usually inadvertently changed in artificial weathering devices. The condensation, fog, immersion, or water spray used to create moisture can introduce oxygen to the test environment and the surface of the panels. Even in natural weathering, oxidation of a coating surface usually occurs in the presence of moisture.

Oxidation involves breaking bonds within a cured coating. Either primary or secondary bonds may be affected by oxidation. Since the oxidation process is different for different chemical types (acrylic, epoxide, vinyl, etc.) of coatings, the results of oxidation can range from embrittlement to softening along with crazing, cracking, or discoloration. Oxidation usually begins as a surface phenomenon that breaks down the outer polymeric binder layers. Water can then pass through the film to the inner layers and cause further breakdown (often at an accelerated pace) of binder and additives.

Other Factors

Although light, heat, moisture, and oxygen play important roles in the deterioration process, it should be recognized that there are other factors that affect coating stability. Weather resistance is dependent on the curing or drying process, the substrate being painted, and application methods. These conditions cannot be fully simulated under controlled laboratory conditions since, as with natural weathering, these conditions are seldom the same.

In actual service, most coatings experience environmental factors that often continually change, are not reproducible, or are unforeseeable at the time of application. Examples are acid rain or other transient environmental pollutants. Chemical exposure, particularly in the vicinity of chemical plants or other heavy industrial environments, can also contribute to degradation. Testing for chemical resistance is discussed elsewhere in the manual.

ACCELERATED WEATHERING DEVICES

Carbon Arc and Xenon Arc

Carbon arc and xenon arc lamp devices are used to expose specimens to UV radiation, elevated temperature, and water spray. Carbon arc apparatus principles and operating procedures are given in ASTM Practice for Operating Light-Exposure Apparatus (Carbon Arc Type) With and Without Water for Exposure of Nonmetallic Materials (G 23), and the test conditions for paint and coatings are outlined in Practice for Conducting Tests on Paint and Related Coatings and Materials using Filtered Open-Frame Carbon-Arc Light and Water Exposure Apparatus (D 822). The basic principles and operating procedures for xenon arc devices are found in ASTM Practice for Operating Light-Exposure Apparatus (Xenon-Arc Type) With and Without Water for Exposure of Nonmetallic Materials (G 26).

There are several devices manufactured by several companies that use either carbon arc or xenon arc light sources. The basic apparatus is outfitted with one or two carbon arcs or a single xenon arc (Fig. 7). The specimen rack varies in diameter with the diameter dependent on the number or type of lamps used since different rack sizes are used to accommodate the change in irradiance from the different light sources. Samples should be mounted on the rack at a distance such that the location of each sample assures that incident irradiance does not vary by more than 5% from the average. The units usually have automatic temperature controls and may or may not have automatic humidity control. The drum

FIG. 7—Xenon arc weathering device used with permission of A.E.D. Co.

or specimen rack rotates at 1.0 rpm for both the carbon arc and water-cooled xenon arc, and at 2.0, 3.7, or 5.2 rpm for the air-cooled xenon arc to ensure uniform radiation on all samples. Water is sprayed onto the specimens as a fine mist. Exposure to light and to darkness is alternated, and the water spray is intermittent. A blower in the base of the apparatus provides a flow of air through the chamber and over the specimens. The airflow controls the temperature of the samples and removes carbon combustion products. The specimens are mounted vertically on racks above and below the center line of the radiation source. During testing, specimens should be exposed equally from the upper and lower racks.

The light source for these devices should be chosen by the chemical nature of the material to be tested since the spectra of the various light sources are different and produce different weathering results. For both the carbon arc- and the xenon arc-based devices, it is very important to monitor the levels of irradiance at a selected wavelength if the data are to be used for comparison purposes. This is required because there is a progressive decrease in radiation intensity as the lamp ages. This can be overcome by progressively increasing the lamp wattage, thereby minimizing the changes in intensity, and by monitoring the radiation output as described in ASTM G 26. The newer devices monitor and automatically adjust the wattage to keep the intensity constant.

Both carbon arc and xenon arc procedures include four test methods:

1. Continuous exposure to light and intermittent exposure to water spray.
2. Alternate exposure to light and darkness and intermittent exposure to water spray.
3. Continuous exposure to light without water spray.

4. Alternate exposure to light and darkness without water spray.

A typical cycle used for evaluating coatings with these devices is 102 min of light at 145 ± 5°F (63 ± 3°C) and 18 min of light and water spray at 60 to 63 ± 2.5°F (15.5 to 17 ± 1.5°C).

Fluorescent UV/Condensation

With fluorescent UV bulb devices as described in ASTM Practice for Operating Light- and Water-Exposure Apparatus (Fluorescent UV-Condensation Type) for Exposure of Nonmetallic Materials (G 53), specimens are cycled between exposure to UV light and condensation in a heated environment (Fig. 8).

The light source for the QUV [*8*] and UV-CON [*9*] is composed of eight fluorescent lamps that produce light in the ultraviolet range. The light source may be any of the UV fluorescent bulbs produced. The particular bulb used will determine the nature and speed of results acquired. The exterior of the specimen rack is exposed to room temperature, and the inside is exposed to heat and humidity produced by the lights and a heated water bath. The condensation is caused by the temperature differential that exists between the front and back of the mounted specimens. The exposure can be varied by changing the temperature, the length of the light, and/or the condensation segments of the cycle. A few models are also available with a spray option. The spray option can be used to simulate thermal shock or erosion by water.

The samples are mounted in brackets, which form the cabinet wall. The panels are stationary and set at an angle so condensate can run off the test surface and be replaced by fresh condensate in a continuous manner. Vents along the bottom of the chamber permit an exchange of ambient air and water vapor to prevent oxygen depletion of the condensate. The specimens are placed approximately 50 mm from the lamps. Both the lamps and the panels should be manually rotated at specified intervals to ensure even UV exposure. To maintain consistent irradiance, the fluorescent lamps are

FIG. 8—Fluorescent bulb/cyclic condensation. Used with permission of the Q-panel Co.

rotated after a specified number of hours with two of the eight being replaced. By rotating the lamps and replacing only 25% of the light source at any one time, an almost constant level of exposure is ensured.

Various test cycles can be selected. If no conditions are specified, ASTM G 53 suggests 4 h of UV light at 60°C and 4 h of dark condensation at 50°C. Test temperatures of 50, 60, and 70°C are widely used.

Fluorescent UV-Salt Fog

The Mebon Prohesion Cabinet [*10*] was originally developed as an alternative to the standard salt fog cabinet, ASTM Test Method of Salt Spray (Fog) Testing (B 117) for conducting corrosion resistance studies (Fig. 9). Recently it has been suggested for use as an accelerated weathering device when used in conjunction with a fluorescent UV condensation device [*11*].

The Prohesion Cabinet introduces a spray or fog by means of an external reservoir and a peristaltic pump operating at a flow rate of from 0.5 to 1.5 mL/h. Although a variety of solutions can be used, one consisting of 0.4% ammonium sulfate and 0.05% sodium chloride (Harrison's solution) is recommended for corrosion studies. A series of experiments with this device indicated that, at least for corrosion rate studies, this solution provided more realistic results than the warm, 5% sodium chloride solution used in salt fog cabinets [*12–14*]. The conclusion that these test results were more realistic was based on an analysis of the corrosion products. This analysis revealed that the amount of sulfur and chlorine salts on panels exposed to the particular salt solution was similar to the amount and type found on the panels that had been corroded at an outdoor location.

The fog, introduced at ambient temperature, is eliminated by forcing air through the device at 23 to 55°C. Not only does this assist in drying the panels, it also replenishes the oxygen. The wet-dry cycles can be varied from 1 to 10 h. Since the cabinet is not outfitted with a light source, it is necessary to manually move the panels from the Prohesion Cabinet to a fluorescent UV/condensation device to incorporate the element of light into the test.

UV Light-Cyclic Immersion

A proposed ASTM method entitled "Standard Practice for Conducting Cyclic Immersion/Atmospheric Exposure Tests" is currently being developed. Its intended use is for the cyclic testing of specimens, either manually or automatically, through an atmospheric environment and an immersion environment. The atmospheric environment may consist of light, heat, air, and/or chemical gases or fumes. The immersion portion of the cycle varies and is dependent on the construction material used to make the individual devices. In addition, the liquid may be heated, cooled, oxygenated, and/or filtered.

Cyclic exposure alternates wetting and drying of the samples in combination with UV light. The immersion portion of the cycle allows permeation of the test liquid into the coating. This imbibing of the test liquid may cause swelling of certain coatings and substrates that would not occur during a salt fog or condensation cycle. During the drying cycle, reverse permeation or evaporation may occur, causing the coating to shrink and cause cyclic stressing/straining of the system. Reactions during the immersion portion of the cycle are influenced by the permeability of the coating and require time to initiate. The rate of water/chemical degradation is increased by increased temperature. However, long, hot exposures may cause abnormal degradation. The atmospheric exposure after immersion may cause concentration of salts and chemicals on the surface, further increasing the rate of degradation. Care should be taken to select exposure media that approximate those expected during intended service.

FIG. 9—Mebon prohesion cabinet. Used with permission from Q-panel.

The proposed standard currently lists four different devices that meet the requirements. Description of three of the devices follows.

The first device, the Envirotest [*15*], is commonly constructed of stainless steel, but a model constructed of polyethylene is available (Fig. 10). The chamber contains a center axle with spokes for sample mounting. The lower half of the test chamber contains the immersion solution. Four fluorescent bulbs with a heating element are contained in the upper half of the chamber. The type fluorescent bulb, UVB-313, UVA-340, or FS-40, should be chosen by the nature of the specimens to be tested. The distance of the samples from the light source can be varied slightly by moving the sample mounts, but they should remain constant during the testing period.

The chamber is fitted with ports in both the atmospheric and immersion sections. The ports are used for exhausting, draining, and/or recycling liquids or gasses. These ports also allow the immersion solution to be heated, cooled, filtered, and/or oxygenated during the test without disturbing the cycle. The immersion solution may be deionized, fresh, or salt water, acid solutions, or alkali solutions.

The device allows use of a variety of UV light/immersion cycles and immersion solutions. However, a default cycle is rotation at a speed of 20 rpm, a rotation distance of 420°, a pause of 4 h, a temperature of 140°C, and an immersion solution of tap water.

The second device, the QUV/HO [*16*], is constructed of corrosion-resistant materials and encloses eight fluorescent UV lamps, a heated water pan, specimen drawers, and provisions for deionized water spray. The samples are alternately exposed to UV light, water spray, condensation, and immersion.

The immersion cycle is produced by water spray collected in the specimen drawers. The depth of immersion is controlled by the time duration of the water spray and by plugging overflow holes to a desired depth. The specimens are set at an angle to produce a shoreline effect during the immersion cycle. The drying cycle is accomplished through heat generated during the UV cycle and evaporation.

Various test conditions can be used, but the default cycle is 6 h at UV light exposure at 60°C, 2 min of water spray, 6 h of condensation at 50°C, and a maximum level of ponding water covering half of each sample. The UV light source may be any of the fluorescent bulbs and should depend on the material being tested. The spray is limited to water at this time.

The third device is the Sunchex apparatus [*17*] is constructed of corrosion-resistant material and is suitably sized for tabletop operation. An air-cooled xenon arc lamp and a horizontal specimen tray are housed in the device. When in test operation, specimens are alternatively exposed to UV light, water, immersion, and heat.

The immersion cycle is produced by a continuous water flow over the specimen for a variable amount of time. The water depth has a maximum of 0.75 in. (1.9 cm). The dry cycle is accomplished by pumping the water from the specimen tray. The UV light exposure is provided by the 1500-W lamp that is mounted approximately 21 cm above the specimen tray. Uniform radiation distribution over the samples is achieved by the use of parabolic reflectors, glass optical filters, and reflective materials on the chamber walls.

Various test conditions can be used. The light cycle is variable from 1 to 999 min, and the immersion and dark periods can be varied between 1 and 99 min. A default cycle for paint test has not been developed since this device is currently being used in the plastic, rubber, and textile industries.

Fresnel Reflector

There are three methods for accelerating natural weather exposure: black box, heated black box, and fresnel reflector. These are described in ASTM Practice for Conducting Accelerated Outdoor Exposure Tests of Coatings (D 4141). The

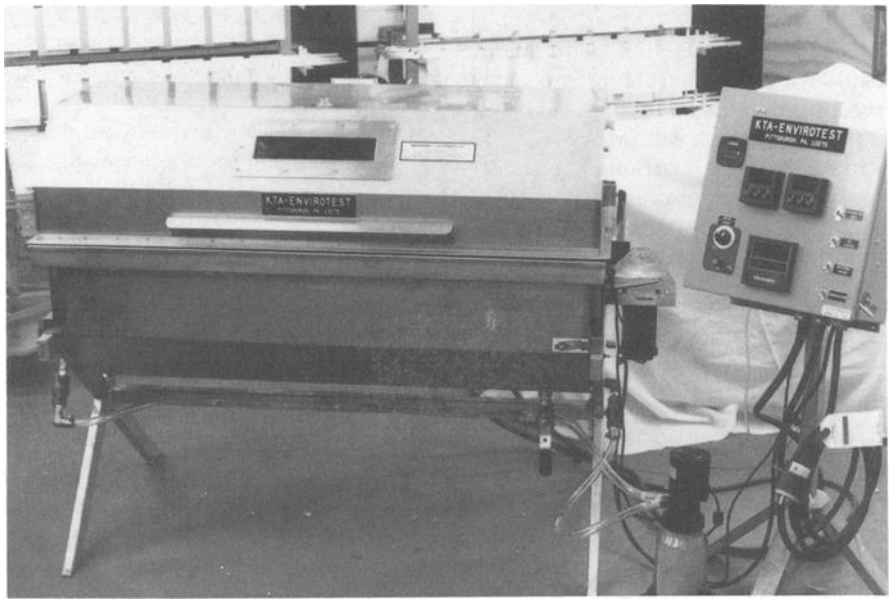

FIG. 10–Cyclic immersion/fluorescent bulb. Used with permission of KTA-Tator, Inc.

first two methods accelerate the weathering by increasing the temperature of the exposed surface and are discussed in the natural weathering section. The fresnel reflector is the only method that collects and intensifies natural sunlight to accelerate weathering. The basic principles for this method are found in ASTM Practice for Performing Accelerated Outdoor Weathering of Nonmetallic Materials Using Concentrated Natural Sunlight (G 90). It is performed in the desert region of Arizona using Sun-10, FRECKLE, EMMA, EMMAQUA, or other similar devices that involve the use of a mirror array [*6,18*]. A more detailed description of this device is presented in the chapter that deals with natural weathering.

The concentration of sunlight is achieved by collecting sunlight on ten mirrors and focusing the reflected light onto the specimen. The assembly is designed to actually follow the track of the sun as it moves through the sky. The device is equipped with a blower to regulate the surface temperature of the specimen. The maximum surface temperature that can be reached is limited to no more than 10°C above the maximum temperature normally achieved by natural weathering. The test may be performed with or without water spray. The water spray is provided by an oscillating nozzle assembly, which supplies deionized water as a fine, dense mist. The water is sprayed on the samples for set cycle times. A common cycle is 8 min of water spray per hour. Exact cycles are given in ASTM G 90.

Since this method uses natural sunlight, the spectrum produced follows that of natural sunlight but at a higher intensity level (Fig. 11). The testing can be performed for specific levels of solar exposure or for specific time periods. The quantity of light is measured by a radiometer, and it is expressed as total solar radiant exposure. The preferred method is based on solar exposure since this accounts for the natural seasonal variations of sunlight. This allows, for example, results obtained in January to be directly compared to those obtained in July.

Ultrafast Weathering

In contrast to all of the above methods, this technique of ultrafast weathering does not wait for visual changes to occur on the surface. At the present time, this method is still being evaluated to determine if there is any correlation between the information gathered using electron spin resonance (ESR) spectroscopy to monitor radical formation and natural weathering results [*2*]. The theory behind ultrafast weathering is based on the assumption that the radicals which form within the first several hours of the test will reveal the relative stability of the coating. For this testing, the process of radical formation is induced by ultraviolet radiation greater than that of sunlight. The light is filtered to remove unwanted shorter wavelengths and also focused on the sample using a cooled mirror. The sample is placed between the poles of a magnet in the microwave resonator of the spectrometer. The radical formation is plotted as a function of light-exposure time. Each paint will produce a characteristic curve. If a correlation is found to exist, the curves of different paints are then to be compared to determine which exhibits the best UV light stability. This testing could be completed over several hours instead of days, months, or years.

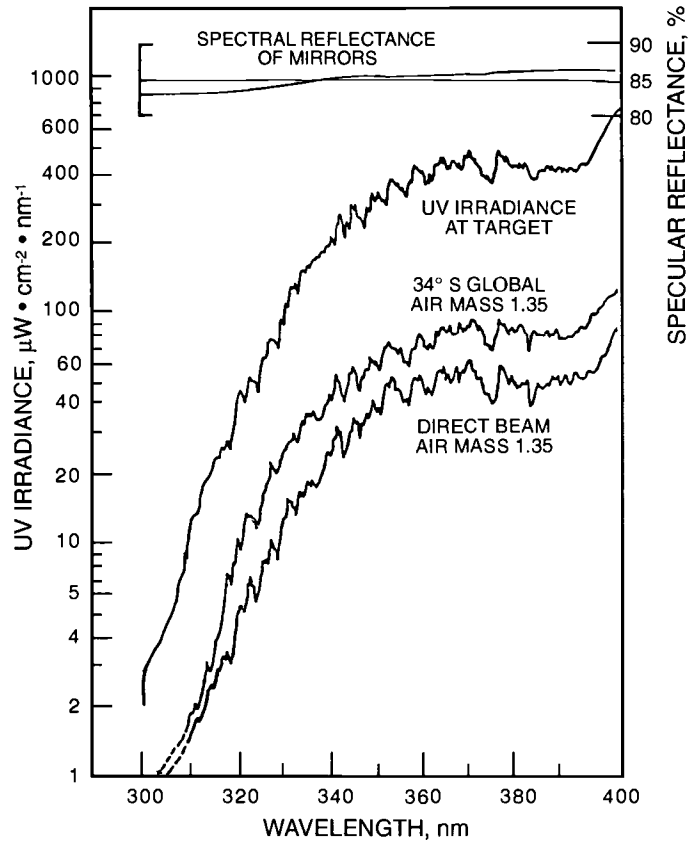

FIG. 11–Spectrum of light produced by fresnel-reflector testing devices.

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[*8*] ASTM has found suitable devices available from Atlas Electric Devices Co., 4114 Ravenswood Ave., Chicago, IL 60613 and from Quartzlampen GmbH, 6450 Hanau/Main, Germany (domestic distributor is Batson Machinery, Inc., P.O. Box 3978, Greenville, SC 28608).

[9] ASTM has found suitable devices available from Q-Panel Co., 26200 First Street, Cleveland, OH 44145 and from Atlas Electric Devices Co.

[10] Licensed by Mebon Limited, Nottinghamshire, England to Q-Panel Co., 26200 First Street, Cleveland, OH 44145.

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[15] ASTM has found suitable devices available from KTA-Tator, Inc., 115 Technology Drive, Pittsburgh, PA 15275.

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Biological Deterioration of Paint Films

by David L. Campbell[1]

DESCRIPTION OF THE PROBLEM

Water-borne liquid paints can experience viscosity loss, putrefaction, gas formation, color change, and pH drift as a result of the degradation of some or all of the organic constituents [*1*]. This deterioration can be caused by bacteria or fungi-releasing enzymes in the paint or by enzymes which have been introduced into the paint through contaminated raw materials or equipment. Viscosity loss in water-borne paints can also be caused by the presence of oxidants/reductants in raw materials [*2,3*].

Micro- and macroorganisms can destroy both the decorative and protective properties of paint films. Algal and fungal growth can cause discoloration of water- and solvent-borne paint films and ultimately destroy their integrity (Figs. 1 and 2). The susceptibility of paint films to attack by microorganisms is determined in part by the chemical nature of the nonvolatile binder, the choice of pigmentation, and the pigment volume concentration. To a much greater degree, however, the susceptibility or resistance of a paint film to biological attack is determined by the presence and concentration of antimicrobial agents.

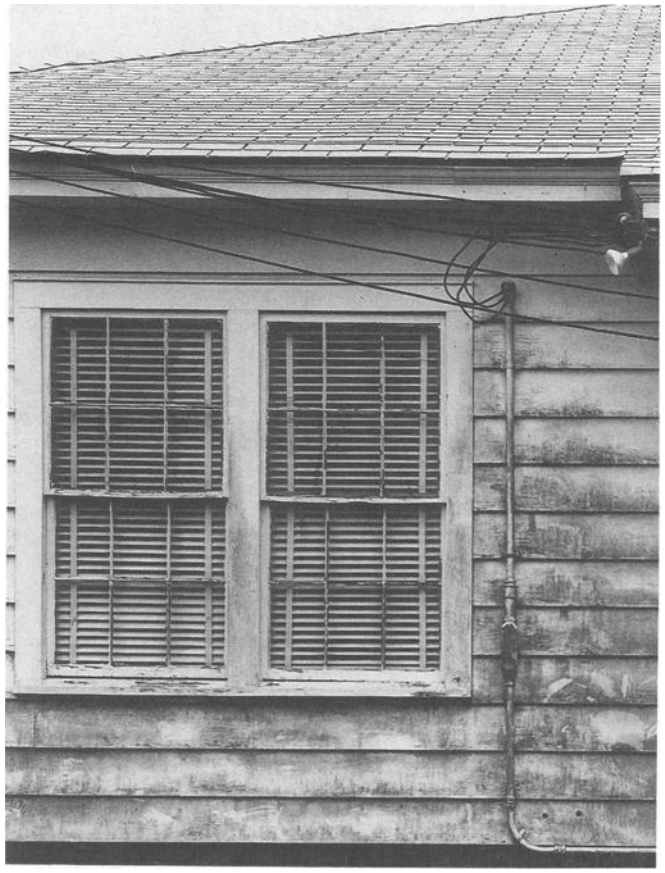

FIG. 1–Fungus discoloration of paint films. Appearance of house one year after painting shows rapid fungal discoloration of paint inadequately protected against microorganisms.

MICROORGANISMS ASSOCIATED WITH PAINT

Microorganisms associated with paint and paint films have been well established. These organisms include bacteria, fungi, and terrestrial algae.

The bacteria genera *Pseudomonas, Aerobacter, Enterobacter, Flavobacterium,* and *Bacillus* are frequently isolated from spoiled paints [*4,5*]. Of these, the *Bacillus* are unique in that, under conditions of stress such as heat, cold, or dehydration, some are able to form spores which are resistant to high temperatures and dry environments and more resistant to bactericides. Opperman and Goll [*6,7*] found anaerobic bacteria in contaminated water-borne paints and raw materials. The aerobic culture methods commonly used would not detect the presence of these bacteria, which are capable of utilizing organic paint components as nutrients.

Fungi are present on the surface of paint films in two forms. They may be present as thread-like structures technically referred to as mycelia or as clusters of spherical, usually black-colored, spores. These two different appearances of fungi have been popularly labeled the trees and fruit of fungi. In reality, they represent the two different growth forms in the life cycle of fungi. The mycelial structures are observed when the fungi are actively growing and reproducing. Spore clusters are found when conditions for growth and reproduction are less favorable. Spores are more resistant to environmental changes and antimicrobial agents than are the mycelial forms. Spores and spore clusters are frequently difficult to differentiate from soil or soot particles. Examination with a magnifying lens or microscope is frequently necessary for positive identification by even the skilled microbiologist. Photomicrographs of the two different forms of fungal growth are shown in Figs. 3 and 4.

[1]Project manager, Technical Center, Rust-Oleum Corporation, 8105 Fergusson Drive, P.O. Box 70, Pleasant Prairie, WI 53158-0769.

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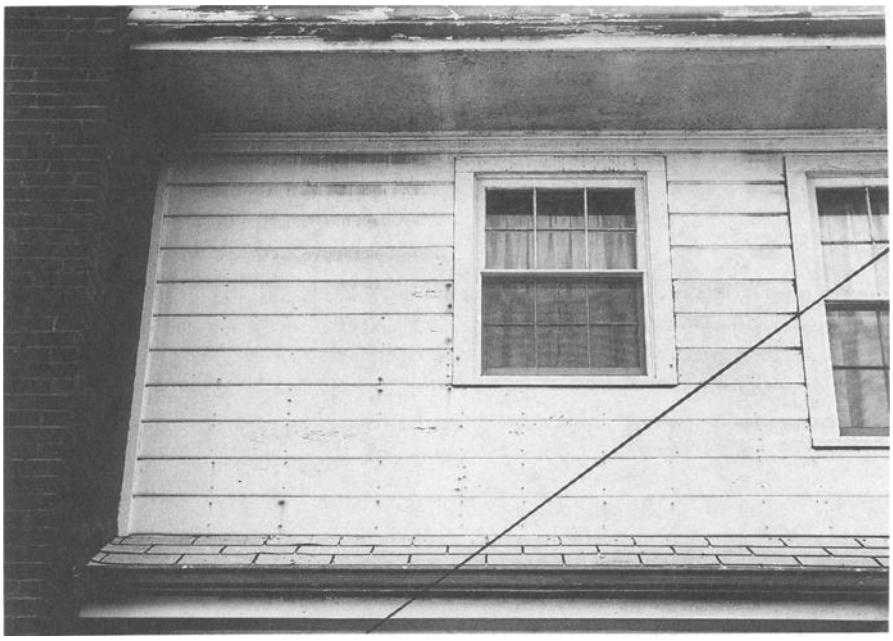

FIG. 2–Fungus disfigurement of paint films. Appearance of house three years after painting. Chalking of the paint has physically removed fungus from vertically exposed areas, but, in absence of chalking under the eaves, fungus growth has continued and showed an inadequately preserved paint.

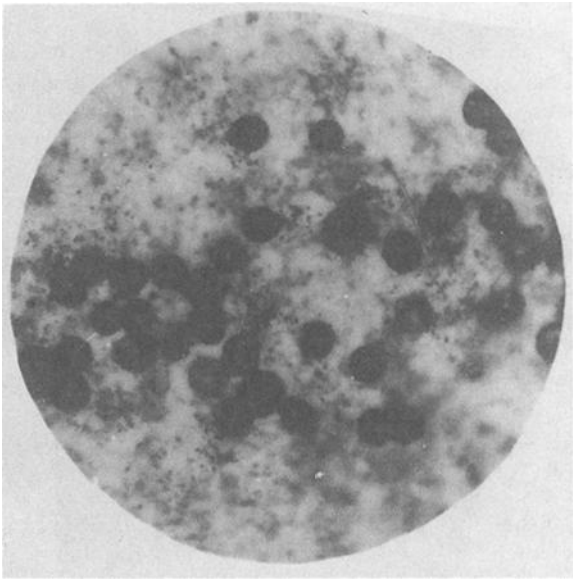

FIG. 3–Spores of fungus on a paint film. Magnification ×150.

Numerous fungi are found on and within paint films, although a few predominate. Goll and Coffey [*8*] were the first to observe and report the wide-spread growth of *Aureobasidium pullulans*. In isolation studies of oil and alkyd paint films at six wide-spread geographical locations, Rothwell [*9*] confirmed the predominance of *Aureobasidium pullulans* but noted the close resemblance of, and predominance in certain geographical areas of *Cladosporium* species (sp.). Other fungi frequently isolated include *Alternaria dianthicola* and *Phoma pigmentivora*. The same studies indicated the consistent presence of bacteria within the paint film and at the paint-wood interface. *Flavobacterium marinum* was by far the predominant bacterium isolated. Despite the differences in the chemical nature of latex emulsion binders, Drescher [*10*] isolated essentially the same microorganisms from latex emulsion paint films exposed at the same location.

The microflora of interior paint films in breweries, dairies, canneries, and other food-processing plants were reported by Krumperman [*11*] and included many fungi rarely found on exterior paint films (Fig. 5). Prominent among these are *Aspergillus* sp. and *Penicillium* sp. Found to a lesser extent were *Cladosporium* sp. and *Aureobasidium pullulans*. His investigations again indicated the frequent occurrence of the bacillus *Flavobacterium marinum*.

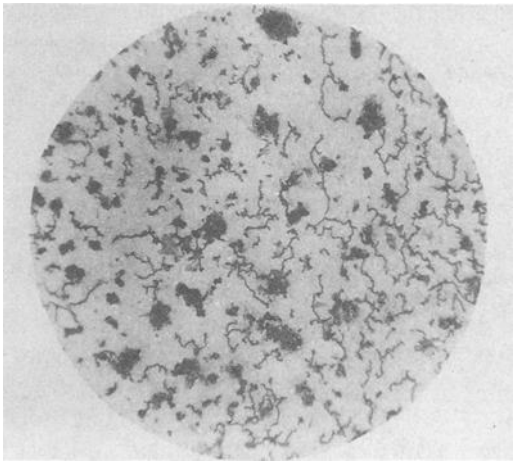

FIG. 4–Mycelia of fungus on a paint film. Magnification ×75.

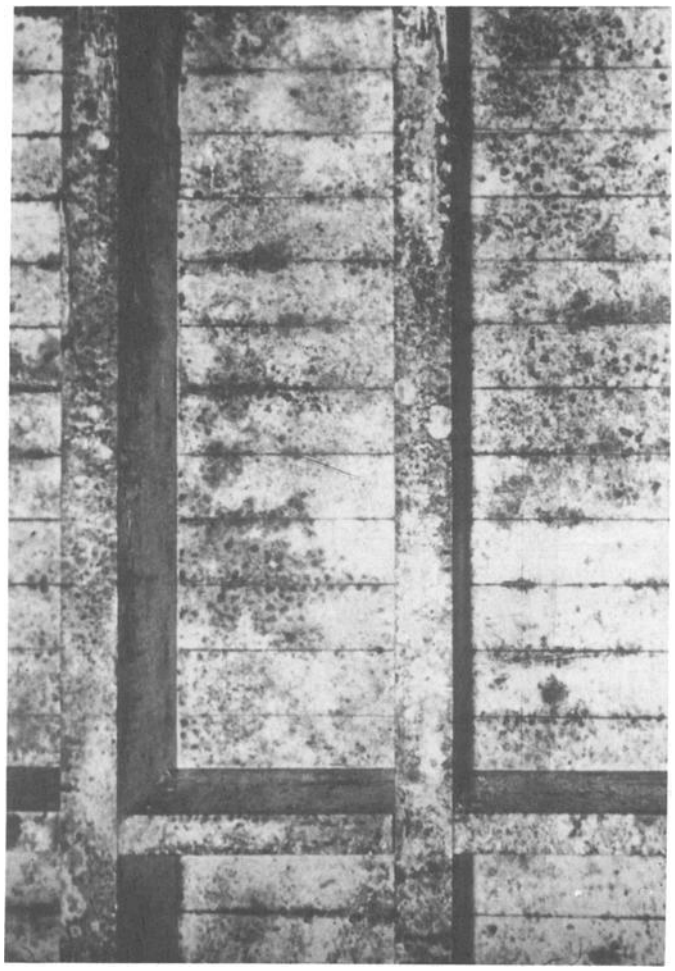

FIG. 5–Fungus disfigurement of paint films. Appearance of ceiling in a food processing plant only six months after painting. The high humidity and the nutrients supplied by food processing create an environment especially favorable to growth of fungi.

Algae, which contain chlorophyll, manufacture their own organic carbon from atmospheric CO_2 and light energy in photosynthesis. The nuisance growth of terrestrial algae on painted surfaces has been described by Skinner [*12*] and Drisko et al. [*13*]. The Cyanobacteria (blue-green algae) *Oscillotoria* sp. and *Scytonema* sp. predominate in tropical conditions. Algae may be filamentous or unicellular organisms and vary in color from green to brown to black. The green alga *Protococcus* sp. (*Pleurococcus*) is prevalent in the temperate climates (Fig. 6).

DETERMINING THE PRESENCE OF FUNGAL OR ALGAL GROWTH ON PAINT FILMS

When doubt exists as to whether the defacement is due to algae, fungi, or dirt, the surface can be examined using magnification of ×10 to ×100 to distinguish among fungal, algal, or dirt disfigurement as described in the ASTM Test Method for Evaluating Degree of Surface Disfigurement of Paint Films by Microbial (Fungal or Algal) Growth or Soil and Dirt

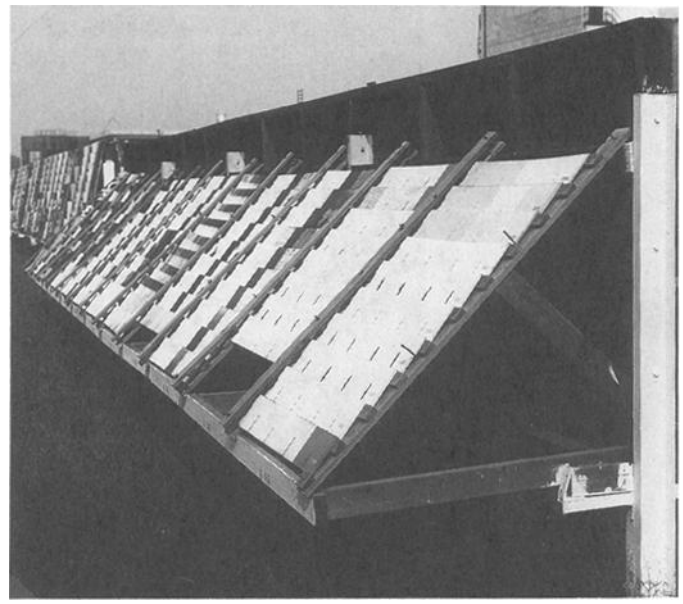

FIG. 6–Test fence exposure of paints. Specimens are placed 5° off vertical and are offset so that runoff from higher specimens does not contaminate specimens below. This arrangement allows different paint to be applied to each panel.

Accumulation (D 3274). Photographic reference standards for rating the disfigurement of paint films are illustrated in this method.

The composition of fungi and algae permits the use of chemical identification. The ASTM Guide for Determining the Presence of and Removing Microbial (Fungal or Algal) Growth on Paint and Related Coatings (D 4610) contains procedures for chemical, visual, and subculture determination of fungi and algae. The chemical procedure uses 5% aqueous sodium hypochlorite solution applied to the disfigured area of the film with bleaching as an indication of algae or fungi. The test has its limitations and thus should be interpreted with some degree of caution. Insect eggs or fecal material will bleach since both are composed of protein. The test should be limited to white or light-colored paint since on deeper-colored paint films the bleaching of fungal or algal growth may be insignificant compared to that of the paint. Moreover, a heavy chalk face interferes with the test, and areas discolored by metal may give false results. ASTM D 4610 therefore contains the visual and subculture procedures which can be used for confirmation of the chemical test results. A subculture may be made by applying a prepared petri dish containing a raised convex surface of nutrient agar culture medium directly to the surface to be sampled and exerting moderate pressure. Replace the cover and incubate for 72 h at 98°F (36.7°C). Examine the agar surface visually in accordance with ASTM D 3274. The culture medium must contain the nutrients necessary for growth of algae or fungi.

ANTIMICROBIAL AGENTS

Chemical agents used to control or prevent the deteriorating effect of microorganisms are referred to as *microbistats* if they do not kill microorganisms but prevent their reproduc-

tion and as *microbicides* if they kill microorganisms. Most of the microbistats and microbicides used in paint films effectively control fungi, algae, and bacteria by interfering with their metabolic functions.

Table 1 lists more frequently employed antimicrobial agents used in paints as bactericides, algicides, or fungicides as recommended by the manufacturers.

DETERMINING MICROBIOLOGICAL RESISTANCE OF PAINTS

The microbial resistance of paints and paint films is an important characteristic of such paints, and considerable attention has been given to developing laboratory and field tests that will predict the resistance of paints to biodeterioration. Some of the tests require the use of pure culture microorganisms. Those employed are listed in Table 2 and may be obtained from: American Type Cultures Collection, 12301 Parklawn Drive, Rockville, Maryland 20852. Many tests employ synthetic growth media. These are summarized in Table 3.

The more commonly employed tests include the following.

TABLE 1—Antimicrobial agents used in paints and paint films.

ALGICIDES
diiodomethyl-p-tolylsulfone
2-methylthio-4-tert.-butylamino-6-cyclopropylamino-s-triazine
FUNGICIDES
diiodomethyl-p-tolylsulfone
barium metaborate
2-n-octyl-4-isothiazolin-3-one
potassium dimethyldithiocarbamate
methylene bis(thiocyanate)
2-(thiocyanomethylthio) benzothiazole
2-(4-thiazolyl)benzimidazole
N-trichloromethylthio-4-cyclohexene-1,2-dicarboximide
zinc dimethyldithiocarbamate
zinc 2-mercaptobenzothiazole
3-iodo-2-propynyl butyl carbamate
tetrachloroisophthalonitrile
N-(trichloromethylthio)phthalimide
tributyltin benzoate
tributyl tin salicylate
tributyltin oxide
zinc oxide
BACTERICIDES
tributyltin oxide
tributyltin benzoate
barium metaborate
potassium dimethyldithiocarbamate
p-chloro-m-cresol
alkylamine hydrochlorides
6-acetoxy-2,4-dimethyl-1,3-dioxane
tetrahydro-3,5-dimethyl-2H-1,3,5,-thiadiazine-2-thione
2 (hydroxymethyl)amino ethanol
1,2-dibromo-2,4,-dicyanobutane
1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride
hexahydro-1,3,5-triethyl-5-triazine
2-(hydroxymethyl)amino-2-methyl-1-propanol
4-(2-nitrobutyl)morpholine
3,4,4-trimethyloxazolidine
4,4-dimethyloxazolidine
5-chloro-2-methyl-4-isothiazolin-3-one
2-methyl-4-isothiazolin-3-one
1,2-benzisothiazolin-3-one
1,3-bis(hydroxymethyl)-5,5-dimethylhydantoin
hydroxymethyl-5,5-dimethylhydantoin

TABLE 2—Microorganism cultures used for test methods.

Test	Microorganism	ATCC Number
ASTM D 2574	*Pseudomonas aeruginosa*	10145
Method 6271[a]	*Aspergillus oryzae*	10196
Nuodex	*Aureobasidium pullulans*	9348
Hutchinson	*Aspergillus flavus*	9643
	Aspergillus niger	9642
	Penicillium funiculosum	9644
ASTM D 3273	*Aureobasidium pullulans*	9348
	Aspergillus niger	9642
	Penicillium citrinum	9849

[a]Federal Test Method Standard 141.

Bacterial Resistance of Liquid Paints

Resistance of emulsion paints in the container to attack by bacteria can be determined in accordance with the ASTM Test Method for Resistance of Emulsion Paints in the Container to Attack by Microorganisms (D 2574). This test predicts the package stability of water-thinned latex emulsion paints as related to bacterial growth in the paint and degradation of organic constituents.

The test consists of two parts. The paint under test is first cultured on tryptone glucose agar to determine if living bacteria are present. A negative result indicates the absence of bacteria but not necessarily resistance to attack. To determine if the test paint can withstand bacterial attack, a specimen of "spoiled" paint containing *Pseudomonas aeruginosa* is introduced into the test paint, and the latter is incubated at room temperature for a period of six weeks. At intervals of 24, 48, and 72 h and at one-week intervals for the remainder of the test period, the inoculated test paint is streaked on tryptone glucose extract agar slants. The test paint is reported to be resistant to bacterial attack if no living organisms can be recovered through six weeks of incubation. Conversely, the paint is reported to be "not resistant to bacterial attack" if living bacteria are recovered at any time during the incubation period. The principal difference between the ASTM test and previously employed tests of this type is the use of "spoiled" paint as an inoculum, rather than aqueous suspensions of bacteria removed from laboratory growth medium. By employing paint containing *P. aeruginosa*, already adapted to a paint environment, the shock of a drastic environmental change is eliminated. Repeated inoculations may be necessary to obtain a "spoiled" paint for use as an inoculum, but once prepared, it can be maintained indefinitely.

Measuring the Fungal Resistance of Paint Films

The inability to duplicate the use environments of exterior and interior paint films has made it difficult to develop suitable accelerated tests for the evaluation of their fungal resistance. Most laboratory tests have been based on the widely used agar plate method or modifications of it. Simply described, the agar plate test consists of placing a painted substrate on a bed of agar, inoculating the system with the test

TABLE 3—Formulae of growth media for bacteria and fungi.

Ingredient	Tryptone Glucose Extract Agar[a]	Federal Test Method 6271	Malt Agar[a]	Hutchinson	Zabel
$NaNO_3$	...	3.0 g	...	...	...
NH_4NO_3	...	...	...	1.5 g	...
NH_4SO_4	...	...	...	...	1.47 g
KCl	...	0.25 g	...	0.5 g	...
$MgSO_4$-$7H_2O$	...	0.5 g	...	0.5 g	0.5 g
KH_2PO_4	...	...	...	...	10.0 g
K_2HPO_4	...	1.0 g	...	1.0 g	0.5 g
Agar	15.0 g	15.0 g	15.0 g	15.0 g	15.0 g
Glucose	1.0 g	...	...	...	10.0 g
Sucrose	...	30.0 g	...	...	...
Malt extract	...	...	30.0 g	...	...
Tryptone	5.0 g	...	...	...	...
Beef extract	3.0 g	...	...	...	...
H_2O to make	1000 mL	1000 mL	1000 mL	1000 mL	1000 mL

[a]Prepared Tryptone-Glucose Extract Agar and Malt Agar may be obtained from Difco Laboratories, Inc., Detroit, Michigan, and Baltimore Biological Laboratories, Inc., Baltimore, Maryland.

organism, and observing growth during a prescribed incubation period.

Federal Test Method Standard 141

Method 6271 (Mildew Resistance) is the agar plate test most frequently referred to in specifications for paints utilized by agencies of the U.S. Government. This method employs sucrose, mineral salts, agar medium, and, in accordance with Federal specifications TT-P-19 (Paint, Acrylic Emulsion: Exterior), *Aspergillus oryzae* is the inoculating organism. The agar medium is prepared according to the recipe shown in Table 3. The pH of the medium may be adjusted to 5.5 to 6.5 with 0.1 *N* hydrochloric acid (HCl) or sodium hydroxide (NaOH). The medium is sterilized in an autoclave for 15 min at 15 lb/in.^{2} (1.034×10^5 Pa) and 121°C. Approximately 30 mL is poured into each sterile petri dish and allowed to harden.

The inoculum is prepared by adding 10 mL of sterile water containing 0.005% nontoxic wetting agent such as Tween-80 to a tubed subculture of *A. oryzae*. The mixture of spores and mycelia are removed by gently stroking the agar surface with a sterile camel's hair brush. The aqueous suspension is removed and diluted with sterile water to 100 mL.

The test paint is brushed on each side of a sheet of Whatman filter paper No. 3.0, or equivalent, and allowed to dry for 24 h. Squares of the painted filter paper, 1.25 in. (3.18 cm) on the side, and with guide lines of waterproof ink ⅛ in. (0.32 cm) from each edge, are centrally placed on the agar surface of each dish. Using a sterile pipet, 1.0 to 1.5 mL of the diluted spore-mycelial inoculum is distributed over the painted surface and surrounding agar surface. Duplicate plates should be prepared. The inoculated agar plates are incubated for seven days at 28 to 30°C and 90% relative humidity. At the end of the incubation period, the specimens are examined visually at ×1 and approximately ×18 magnification. Fungal growth on the agar surface or on the edges of the painted filter paper is ignored, and such specimens are considered to pass the test if free of growth within the guidelines.

Nuodex Method

In order to improve the accuracy of the mildew test as required by the exterior paint Federal Specification TT-P-19, Nuodex laboratories modified the test as follows: *Aureobasidium pullulans* replaced *Aspergillus oryzae* because it is the fungus most frequently isolated from exterior house paints. Malt-extract agar replaced the sucrose-mineral salts agar because, in it, *A. pullulans* exhibits growth forms typically observed on exterior paints rather than yeast-like forms that it exhibits when grown on the sucrose-mineral salts agar.

Hutchinson Method

The Hutchinson Method [*14*] is similar to the Federal Method 6271, but employs glass string rather than filter paper as the paint substrate, a liquid broth culture media containing no carbon source and a mixed suspension of *Aspergillus niger, Aspergillus flavus,* and *Penicillium funiculosum.*

ASTM Test Method for Resistance to Growth of Mold on the Surface of Interior Coatings in an Environmental Chamber (D 3273)

This test is used to evaluate the resistance of interior paint films to fungus attack and reportedly provides more accurate results by virtue of removing the artificial aspects of the previously described laboratory method. Test paints are applied to either white pine or gypsum board panels measuring 3 in. (7.0 cm) by 4 in. (10.2 cm) by 0.5 in. (1.3 cm). Two coats of paint are applied to both sides and all edges of the panels at a spreading rate of 450 ft/gal (11.1 m/L) per coat. The specimens are then conditioned at 75°F (24°C) and 50% relative humidity for four days after application of the last coat before being placed in the test chamber. The chamber may be any cabinet capable of maintaining a relative humidity of 95 to 100% and a temperature of 90°F (32°C) and large enough to accommodate specimens, a water bath, and a soil bed that serves as an inoculum source. The soil bed is constructed of a stainless steel or plastic tray with a monel mesh bottom (16 mesh). The soil employed is a good quality, green-

house grade potting soil containing 25% peat moss. The pH of the soil is maintained between 5.5 and 7.6. The soil is inoculated with spore and mycelium suspensions of *Aureobasidium pullulans, Aspergillus niger,* and *Penicillium* sp. prepared from 10 to 14-day-old agar slants. At least 14 days should be allowed for the fungi to sporulate prior to beginning any tests.

Panels can be placed in the cabinet at any angle desired. Inoculation of the paints is accomplished naturally by airborne spores. To maintain a continuous inoculation, a small fan (1/250 HP operating at 300 rpm) is mounted on a wall of the cabinet just above the level of the soil bed and directed over the surface of the soil. By virtue of the mesh tray bottom just above the water bath, the soil remains moist to ensure maximum growth of the fungi. The test panels are rated for fungal growth over a four-week period. When operating properly, unpainted wood panels or paints containing no antimicrobial agent should develop a 4 to 6 mold growth rating within two to three weeks. The advantage of the environmental chamber method is its close duplication of use conditions.

Zabel Test

The Zabel Test [*15*] was developed to overcome the difficulty in achieving the growth of *Auseobasidium pullulans* in the ASTM environmental chamber. The procedure involves five major steps: (1) the preparation and treatment of partially painted wood specimens; (2) the preparation of stain chambers; (3) sterilization of the specimens and assembly in the stain chambers; (4) inoculation of the painted wood and incubation; and (5) disfigurement evaluation.

Specimen Preparation and Treatment

Flat strips of veneer (7.5 cm long, 3.0 cm wide, and 0.5 cm thick) are cut from the sapwood of southern yellow pine. The strips are heat sterilized for 20 min at 121°C, cooled, and then painted by brushing one heavy coat on the upper half of one surface. After the paint has set and hardened (two to three days), the strips are soaked in distilled water for 15 min, placed individually in Petri plates supported on small glass rods (or placed individually in large glass tubes and cotton stoppered) and surface sterilized by steaming for 15 min in an autoclave at 100 to 101°C. The painted specimens are then ready for introduction to the stain chambers.

Stain Chambers

The stain chambers are screw cap 16-oz French square bottles. These are vertically positioned, and 20 g of vermiculite are added.

The agar medium is prepared according to the formula shown in Table 3. A micronutrient solution is prepared as follows: $Fe(NO_3)3.9H_2O$, 723.5 mg; $ZnSO_4{\cdot}7H_2O$, 439.8 mg; and $MnSO_4{\cdot}4H_2O$, 203.0 mg; dissolved in 600 mL of double distilled water, cleared of precipitate with H_2SO_4 (CP grade), and made to a final volume of 1 L. The micronutrient solution is added to the nutrient media in amounts of 2 mL per liter. The micronutrient-enriched nutrient media is then poured into the vermiculite-containing stain chambers (100 mL per chamber). A small square of filter paper is placed on the surface to minimize vermiculite displacement during the pouring, then removed.

Sterilization and Specimen Assembly

The chambers are autoclaved for 40 min at 121°C, stored at room temperature for 24 h and cooled, then reautoclaved for 15 min at 121°C. After chamber cooling, the painted strips are inserted aseptically. The strips are positioned with the painted surface up at about a 15° angle from the vertical and center inserted until the bottom of the painted zone is about 0.5 cm above the vermiculite surface.

Inoculation and Incubation

Spore suspensions of *A. pullulans* (ATCC strain 16624) are prepared by growing the fungus for 14 days at 28°C on malt extract agar (25 g of malt extract and 15 g of agar per liter) plates. Discs (5 mm in diameter) of mycelium are cut from the pigmented margin of the colony and transferred individually into tubes containing 10 mL of sterile distilled water. The tubes are then agitated vigorously for 5 s on a vortex stirrer, forming a uniform suspension of spores and mycelial fragments.

The spore suspension is then aseptically pippetted on the top (5 mL amounts per strip) of the painted zone on the specimens and distributed so it runs uniformly down the painted surface. The spore suspensions should be used within 1 h of preparation. The stain chambers are then incubated at 28°C for 30 days. Darkness is maintained except lighting for occasional observation.

Disfigurement Evaluation

Blue stain development in the wood and fungus growth on the paint are observed and recorded weekly.

Field Exposure Tests

Because of the many different angles of exposure and degree of protection of paint films on houses, buildings, and industrial plants, the only absolutely accurate field exposure test to measure the fungal and/or algal resistance of paint films is the application of the paint on these structures. This is not economically feasible, and thus it has been the practice to apply and expose paints on panels affixed to test racks, providing various angles of exposures (Figs. 6, 7, and 8). See ASTM Practice for Determining by Exterior Exposure Tests Susceptibility of Paint Films to Microbiological Attack (D 3456).

To ensure accurate measurements of fungal or algal resistance, at least duplicate test panels should be mounted so that painted surfaces are exposed both totally to sun and rain and protected from exposure as occurs on the underside of panels exposed at a 45° angle. Paints exposed to the atmosphere should be examined regularly during the period in which the paint shows no chalking, since chalking of paint films frequently physically removes fungus growth from the surface.

Insect-Resistant Paints

While insects do not pose a deteriorative threat to paints or paint films, their attachment to paints following application and prior to the hardening of the paint film presents a serious decorative problem in many geographical areas. Thus, insect-resistant paints are requested continuously, and tests measuring this property are needed. The best-known test for measuring insect resistance of paints is that devised by Westgate

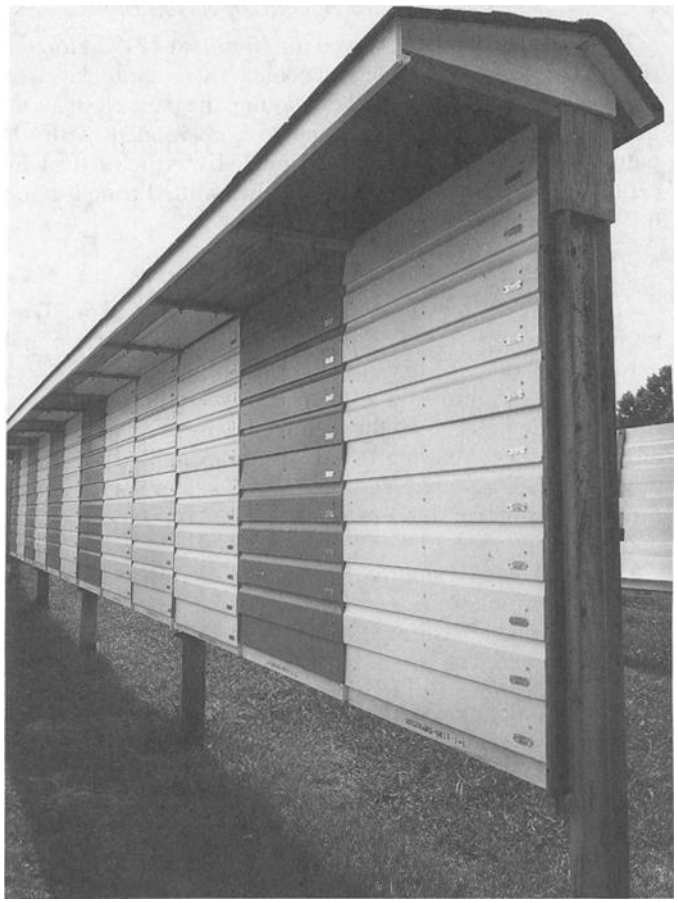

FIG. 7–Test fence exposure of paints. Overhanging eave duplicates house construction and allows evaluation of fungus resistance in both protected and unprotected areas. Because the overlapping siding permits runoff, only one paint system should be used in any vertical area. Compare with Fig. 6.

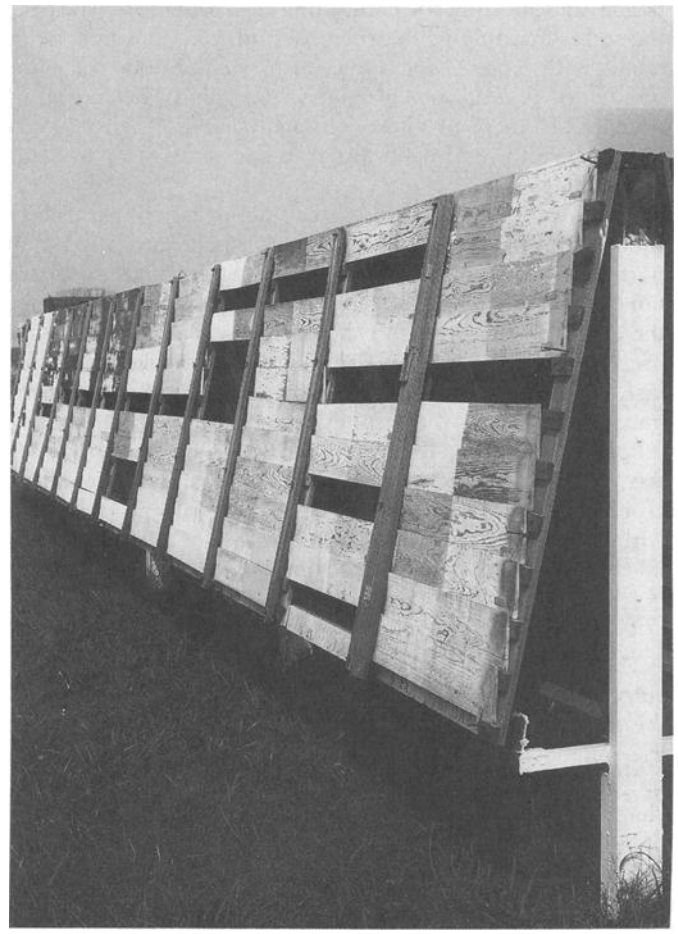

FIG. 8–Test fence exposure of paints. Specimens are placed at an angle of 45° to accelerate weathering comparable to that on roofs, window sills, and other similarly oriented areas. Because of early chalking of paint so exposed, such arrangements are not suitable for evaluation of fungus resistance. However, the underside of 45° exposure provides excellent conditions for evaluating fungus resistance in protected environments.

and Bolton [*16*]. The essential feature of this laboratory method is a lethal chamber from a hiding power sheet, 11½ in. (28.6 cm) by 17½ in. (44.5 cm). The treated paint is applied at a definite spreading rate by means by a doctor blade. The amount, in milligrams, of insecticide per square foot of dry film equals

$$45.4\,WNI/A$$

where

W = weight, pounds, per gallon of paint,
N = percentage of nonvolatile matter,
I = percentage of active ingredient in the nonvolatile portion of the paint, and
A = area, square feet per gallon of paint. Convert to square meters per liter by multiplying by a factor of 0.025.

The sheet bearing the dried film is rolled up to the diameter of a Petri dish and fastened in place with tape. This tube, when capped on both ends with Petri dishes, forms a lethal chamber that may be handled, observed, and stored with ease. It may also be taken apart and given a variety of treatments between tests.

The test insects, for example, the common housefly *Musca domestica*, may be reared from eggs in the laboratory or they may be obtained in the pupal stage from biological supply houses. The flies are transferred most easily from the rearing cage to the lethal chamber by allowing them to fly upwards toward a light. The rearing cage is placed on its back. On the door is placed a sheet of pressed wood containing a hole in which the capped test roll is inserted. A light is arranged above the test roll. The sliding glass door is now pulled out, and the flies stream upward into the test roll. The lower end of the roll is closed with a second Petri dish after the specimen of flies (50 to 100) has been transferred. The flies may be kept under observation during the entire period of contact, which may be terminated within 30 s by blowing the flies into a recovery cage supplied with food. After 24 h have elapsed, the dead and living flies are counted, and the percentage mortality is calculated.

The method has been used to study many of the variables that influence the action of insecticides in paints. Although some insecticide-treated paints show pronounced and prolonged lethal action, the same results may be obtained with

sprays which deposit residues on the paints at a much lower rate of application.

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55

Chemical Resistance

by Alan H. Brandau[1]

THE ABILITY OF A COATING TO RESIST chemical deterioration or staining is an essential element in its evaluation. What follows is a review of established test procedures with various levels of complexity and equipment sophistication that provide a standardized tool for evaluating potential flaws such as discoloration, softening, swelling, adhesion loss, gloss reduction, etc. These tests provide a common ground for crucial communication of performance properties between the manufacturer and end user of a coating. Since these tests are to be representative of actual exposure conditions, it is vital that the tests approximate, as closely as possible, genuine conditions in the field [*1*].

STAINING

Staining tests provide a thorough method of determining the ability of a coating to resist staining from household chemicals, chemical reagents, and other materials common in today's environment. The tests generally expose the coating surface to a spot of the reagent on the coating surface or by immersion of a coated test panel in the reagent for a specified period with timed check points.

Staining from Household Chemicals

Test Method for Effect of Household Chemicals on Clear and Pigmented Organic Finishes, ASTM D 1308, encompasses the evaluation of discoloration, change in gloss, blistering, softening, swelling, loss of adhesion, or other phenomena resulting from a variety of household chemicals. Materials or chemicals suggested as reagents include:

- Distilled water, hot and cold
- Ethyl alcohol, 50% by volume
- Vinegar, 3% acetic acid
- Alkali solution
- Acid solution
- Soap and detergent solutions
- Lighter fluid
- Fruit cut
- Oils and fats
- Condiments
- Beverages
- Lubricating oils and greases

Other materials can also be used as specified by customer or seller. The procedure utilizes open and watch glass covered spot tests with the reagent at ambient temperature as well as immersion tests in the reagent.

Staining in the Transportation Industry

ASTM D 1308, mentioned above, is supplemented by ASTM D 1540, Test Method for Effect of Chemical Agents on Organic Finishes Used in the Transportation Industry. Materials or chemicals suggested as reagents include:

- Glycol-based antifreeze up to 100%
- Acid, alkali, and salt solutions
- Soap and synthetic detergent solutions
- Lubricating oils and greases
- Polish abrasives, creams, and waxes
- Road oils and tars
- Rubber, elastomers, plastics, tapes
- Gasoline
- Water
- Hydraulic fluids
- Alcohol windshield washing solutions

As with ASTM D 1308, discoloration, change in gloss, blistering, softening, swelling, loss of adhesion, or other phenomena are examined after testing. With some reagents, exposure to sunlight or UV light for a specified time is required. Elevated temperature is also used to more closely simulate surface conditions in hot, sunny climates. Gasoline resistance tests combine dripping of fuel at ten drops per minute at a 20° angle with a UV lamp trained on the surface at a 90° angle. Adequate ventilation and safe handling of the dispensing and collecting vessels are essential to safety when working with gasoline. The staining potential of solid materials requires close contact and heat exposure before evaluation.

Staining Resistance of Furniture Finishes

Staining resistance of furniture finishes is covered as part of ASTM D 2571 (Test Methods for Heat-Shrinkable Tubing for Electrical Use), 11.0, Resistance to Oils, Greases, Cosmetics, and Other Household Chemicals. This procedure is concerned with materials such as cosmetics, alcohol, boiling water, and coffee.

Boiling water and hot coffee, prepared by various methods, are poured on a horizontal panel surface and allowed to dry, and the surface is examined for graying, spotting, softening, staining or other film deterioration. Cosmetics are applied to

[1]Vice president, Marketing, Consolidated Research, Inc., 200 E. Evergreen Ave., Mount Prospect, IL 60056.

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the coating surface and placed in a 50°C oven overnight and examined for discoloration or film failure. Fifty percent alcohol or 100 proof vodka is trapped on the coating surface with a watch glass for at least 6 h, allowed to evaporate, and then observed for whitening or spotting that cannot be removed with light polishing with a dry cotton pad.

SOLVENT/FUEL RESISTANCE

ASTM D 2792, Test Method for Solvent and Fuel Resistance of Traffic Paint, relates a method of evaluating the resistance of a coating to solvent and fuel that causes blistering, wrinkling, loss of adhesion, and loss of hardness. The coating is applied to tin panels and air dried for 90 h. Half the panel is immersed in the test liquid, and the vessel is covered for a period of 4 to 18 h as may be specified by the customer. The panels are then removed and examined for defects. The panels are allowed to dry for another 24 h and reexamined for film defects and softening as compared to the unimmersed portion of the control panel.

If subtle differences between coatings are important such as comparative research and development efforts, then the panels can be examined more often without drying at intervals such as 1, 2, 4, 6, 24, and 48 h.

Battelle Chemical Resistance Cell

Several advantages over other immersion methods are claimed for this cell [2], which was developed in the course of research sponsored by Steel Shipping Container Institute, Inc. at Battelle Memorial Institute:

- Panels may be flat or indented
- Edge effects area voided
- Simultaneous testing in liquid and vapor
- Wider range of temperature

The cell consists of a Pyrex glass tube, open at both ends, held horizontally between coated test panels (Fig. 1). A convenient glass tube size is 2 in. (5.08 cm) in diameter and 3 in. (0.762 cm) in length with the ends ground flat. Gaskets are used between tube and panels to give a liquid-tight seal. The frame has screw adjustments for tightening the assembly. A sponge rubber pad behind one panel evens the pressure. A glass ring is used to surround the dimple when an indented panel is under test. The cell is filled through a hole in the middle of the tube. In use, the cell is half filled and stoppered tightly.

Bratt Conductivity Cell for Chemical Resistance

This cell [3], shown in Fig. 2, was designed to use conductivity of a film during chemical resistance tests as a measure of its chemical resistance. The cell proper is a 2-oz vial from which the bottom has been removed, in effect becoming a short piece of glass tubing. The cell is formed by the base plate and an additional plate with a hole that fits over the top of the vial and rests on the shoulder.

During a test, a potential of 15 V is applied to the cell. The metal substrate serves as the positive electrode. The external resistance is selected to produce a voltage drop of about 14 V across the cell.

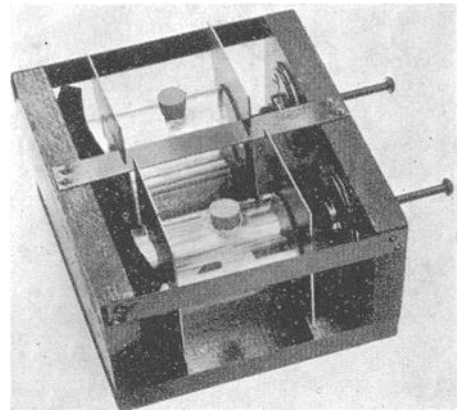

FIG. 1–Battelle chemical resistance cell. (Courtesy of Battelle Memorial Institute.)

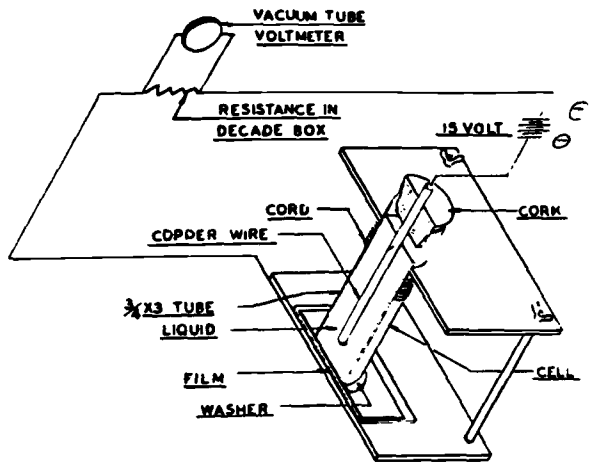

FIG. 2–Bratt conductivity cell. (Courtesy of S. G. Wilson.)

Gearhart-Ball Solvent Resistance

Gearhart-Ball [4] solvent resistance tests utilize free coating films. The cup test employs fastening the free film over the top of a beaker or dish (Fig. 3). Approximately 20 mL of

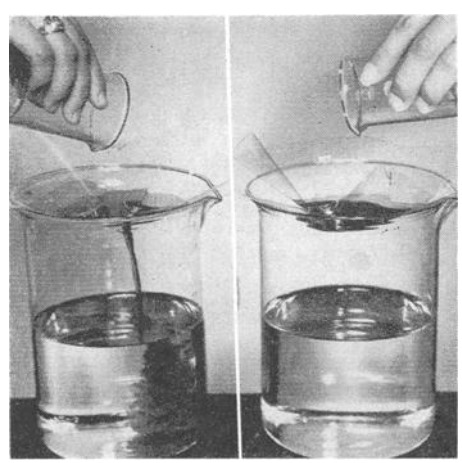

FIG. 3–Cup test for solvent resistance. (Courtesy of F. M. Ball.)

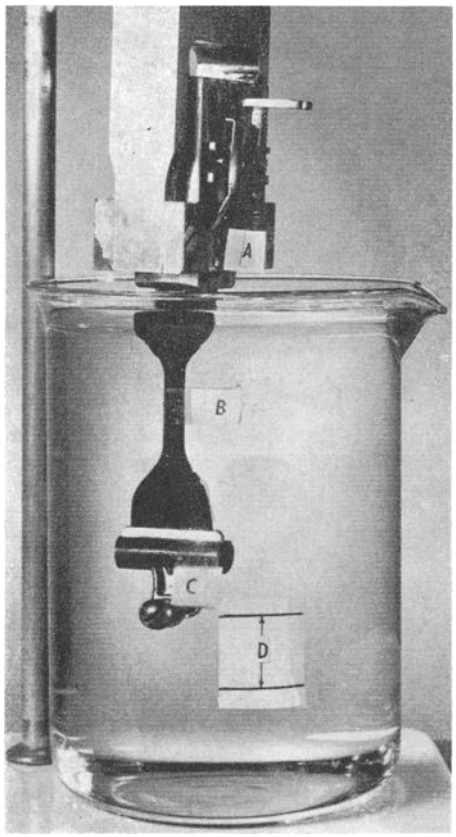

FIG. 4—Distensibility test for solvent resistance. (Courtesy of F. M. Ball.) A = specimen clamp; B = tensile specimen strip; C = alligator clip and weight; D = one inch distance marking.

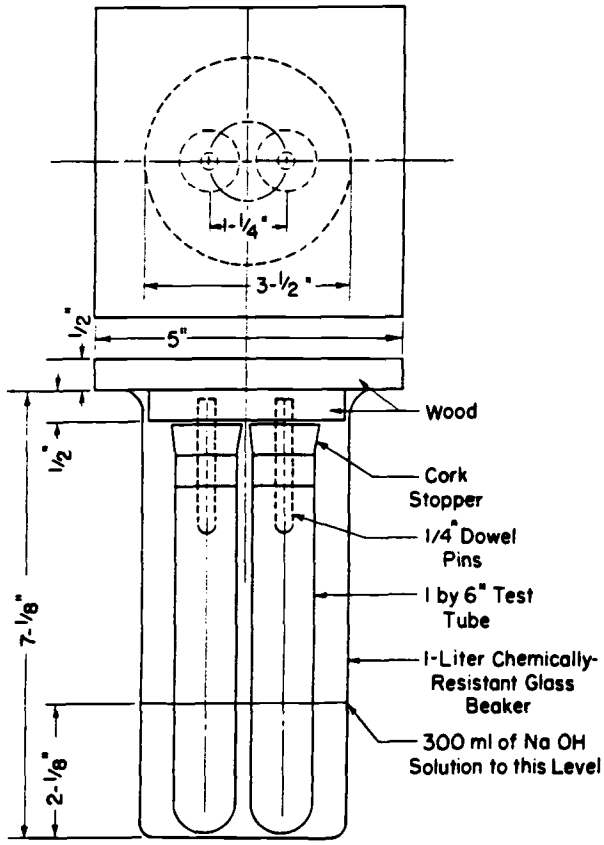

FIG. 5—Apparatus for alkali resistance test.

solvent is poured over the film, and the length of time required to puncture the film is noted. This test would be considered a crude screening test. More precise data can be derived from the distensibility test where a tensile strength strip (see ASTM D 2370.8) is clamped with either a tensile tester jaw or an alligator clip on the upper end, and the bottom end is clamped with an alligator clip with a 12-g weight and immersed in a clear beaker containing the solvent reagent (Fig. 4). The beaker is immediately marked with the initial length, and the time required to elongate the strip one inch is recorded.

Solvent Rub Resistance

Although solvent resistance can be evaluated using ASTM D 1308, many use or adapt a solvent rubbing technique with a gauze cloth soaked in a solvent (MEK is common) and rubbing with the thumb back and forth in 2-in. (5.08-cm) strokes. This procedure, ASTM D 4752, Test Method for Measuring MEK Resistance of Ethyl Silicate (Inorganic) Zinc-Rich Primers by Solvent Rub, is imprecise because the person's strength and the size of the thumb is variable. Nevertheless, it provides a quick relative test without having to wait for exposure results. The MEK resistance of some two-component ethyl silicate zinc-rich primers has been shown to correlate well with the cure of the primer as determined by diffuse reflectance infrared spectroscopy.[2]

ACID RESISTANCE

Acid resistance is determined by exposing a coated panel to freshly prepared mortar as well as a hydrochloric acid solution and is fully described in ASTM D 3260, Test Method for Resistance to Acid and Mortar of Factory-Applied Clear Coatings on Extruded Aluminum Products. The acid resistance test is performed by first sealing the edges of a specially coated panel with a paraffin and beeswax mixture and then

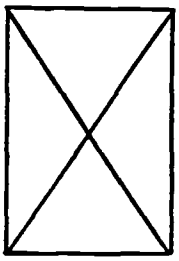

FIG. 6—Q panel is scored with an "x" to expose bare substrate.

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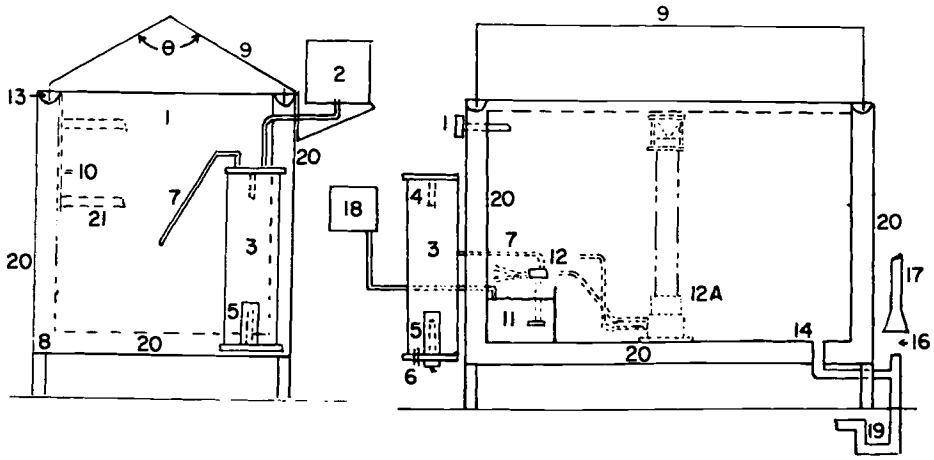

θ—Angle of lid, 90 to 125 deg.
1—Thermometer and thermostat for controlling heater in base.
2—Automatic water levelling device.
3—Humidifying tower.
4—Automatic temperature regulator for controlling heater.
5—Immersion heater, nonrusting.
6—Air inlet, multiple openings.
7—Air tube to spray nozzle.
8—Strip heater in base.
9—Hinged top, hydraulically operated, or counterbalanced.
10—Brackets for rods supporting specimens, or test table.
11—Internal reservoir.
12—Spray nozzle above reservoir, suitably designed, located, and baffled.
12A—Spray nozzle housed in dispersion tower located preferably in center of cabinet.
13—Water seal.
14—Combination drain and exhaust. Exhaust at opposite side of test space from spray nozzle, but preferably in combination with drain, waste trap, and forced draft waste pipe.
16—Complete separation between forced draft waste pipe and combination drain and exhaust to avoid undesirable suction or back pressure.
17—Forced draft waste pipe.
18—Automatic levelling device for reservoir.
19—Waste trap.
20—Air space or water jacket.
21—Test table or rack, well below roof area.

FIG. 7–Diagram of salt-spray (fog) cabinet.

immersing the panel in a 10 vol% solution of 31.6% solution of HCl at ambient temperature for 6 h, followed by rinsing, drying, and examination for blistering, peeling, lifting, crazing, flaking, or discoloration. Mortar resistance is performed by applying a fresh mortar patty, prepared to a specified formula, to both sides of the specially coated panel and then placing in a high relative humidity cabinet for seven days. The mortar is then carefully removed and the panel wiped off with a damp cloth followed by examination as with the acid test.

ALKALI AND DETERGENT RESISTANCE

ASTM D 1308, Test Method for Effect of Household Chemicals on Clear and Pigmented Organic Finishes, is also recommended for evaluating alkali and detergent resistance. It is a simple common sense technique that can be used for many materials or chemicals that can stain or discolor a coating. The choice of testing materials should be related to the coatings end use. As previously mentioned, ASTM D 1308 describes techniques for either immersing the coated substrate in the reagent, putting a small amount of the material on the coated surface and covering with a small watch glass, or just leaving the material on the surface uncovered. The coating is then checked for staining after a period of time or at 1, 2, 4, 6, 24, and 48-h intervals.

For detergent resistance of appliance finishes, a solution of a specified detergent containing a high percentage of sodium phosphate is applied and the temperature maintained at 165°F (73.8°C) for the duration of exposure, usually 250 to 500 h. The test panel is submerged at least six inches into the solution. This is a more severe test than a spot test, but it is more representative of actual service conditions. Examination is done after rinsing and blotting the panel and looking for any manifestation of coating failure.

ASTM D 1647, Test Method for Resistance of Dried Films of Varnishes to Water and Alkali, describes an alkali resistance immersion test using coated test tubes. The use of test tubes coated by dipping into the coating prevents the reagent from creeping under the edge of a flow-on film. As many as 20 tubes are prepared for this test, allowing examination after 1 to 8, 16, and 24 h (Fig. 5). The exposed specimens are rinsed with water and allowed to dry for 30 min before examining for whitening, blistering, or removal of the film.

WATER AND MOISTURE RESISTANCE

There are a number of types of chambers such as moisture chambers, salt fog cabinets, and other accelerated weathering equipment that tests coating moisture resistance as well as other resistance criteria. This type chamber is useful for spot checking accelerated long-term environmental durability. But to be practical, all that is needed to test moisture or water resistance is to partially immerse a coated sample in a glass beaker containing water. The water is maintained at 100°F (37.7°C) for an extended period of time, and the panels are periodically checked for discoloration, whitening, or blistering of the film. The test results are compared to a specification or a standard sample run concurrently. The procedure for this test is ASTM D 870, Standard Practice for Testing Water Resistance of Coatings Using Water Immersion.

SALT FOG TEST

Salt fog resistance is important for marine, automobile, and aircraft coatings and any other exterior coating exposed to salt spray by being near the ocean or exposed to salted road conditions. The severe corrosion caused by salt is well known. The test requires a salt fog cabinet and coated panels. The coating is scored to the bare substrate with a X shape (Fig. 6). The edges are sealed with a weather-proof tape, and the panel is placed in the cabinet for a specified period of time. The metal panels are exposed to the settling fog of an atomized neutral (pH 6.5 to 7.2) sodium chloride solution consisting of 5 parts by weight sodium chloride and 95 parts distilled or deionized water. The sample is then periodically checked to see if the rusted exposed metal has propagated under the coating causing coating failure. As with water resistance, the results are compared to a standard or a specification.

A typical salt spray cabinet as shown in Fig. 7 incorporates a basic chamber, an air saturator tower, a salt solution reservoir, atomizing nozzles, specimen supports, a heater, and controls for maintaining specified temperature. Such chambers are available commercially from several suppliers. The testing procedure, ASTM B 117, Test Method of Salt Spray (Fog) Testing, describes this method in more detail.

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Testing Coatings for Heat Resistance and Flame Retardance

56

by Wayne Ellis[1]

HEAT RESISTANCE

WHEN ORGANIC COATINGS are exposed to elevated temperatures, the initial effect is usually softening, followed by hardening, embrittlement, and degradation. The rate of response and the extent of degradation depend on coating composition, temperature, and length of exposure. There is a distinction in the terminology used to define the resistance of coatings to such changes. Below 400°F (200°C), the property is called "thermal resistance," while above that temperature the property is identified as "heat resistance." Both thermal and heat resistance relate not to occasional heating, but to resistance to change from exposure to a constant heat influence over months or years. Special organic coatings can be formulated to provide thermal resistance, such as those designed to protect steel surfaces exposed to elevated temperature during service life. The upper temperature limit for most organic coatings is in the range of 400°F (200°C). In general, inorganic coatings exhibit better heat resistance than organic coatings. A special group of products are thermal protection coatings, including ablative coatings to protect space vehicles during atmospheric re-entry and intumescent coatings that protect wood or other cellulosic surfaces exposed to fire.

Evaluation of heat resistance is carried out on coated specimens exposed to selected temperatures representative of service conditions and later subjected to other exposure conditions to determine susceptibility to loss of protective function.

ASTM Method D 2485

Typical of this kind of testing is ASTM Test Methods for Evaluating Coatings for High-Temperature Service (D 2485). This method provides an accelerated means of determining performance when coatings are exposed to high temperatures. In Method A, for interior service coatings, coated steel panels are heated for 24 h in a muffle furnace at a selected temperature. One panel is plunged immediately into water for thermal shock, while another is cooled and then subjected to a bend test. In Method B, for exterior service coatings, coated steel panels are heated in a muffle furnace at increasing steps of temperature from 400 to 800°F (205 to 425°C). One panel is subjected to salt spray for 24 h, while another is exposed outdoors for twelve months. When test exposures are completed, the panels are examined and evaluated for film degradation including rust formation, blistering, loss of adhesion, dulling, and chalking.

ASTM Method D 1211

Another test method involving temperature exposure is ASTM Test Method for Temperature-Change Resistance of Clear Nitrocellulose Lacquer Films Applied to Wood (D 1211). A common failure of clear films applied to wood is cracking or checking that may occur over a period of time, either with the grain or at an angle to the grain. This "cold check" test is designed to accelerate the occurrence of checks or cracks by cycling at the temperatures of exposure. In this procedure, which constitutes a single cycle, lacquer-coated wood panels are first subjected to a temperature of 120 ± 5°F (48.9 ± 2.8°C) for 1 h, followed by exposure at −5 ± 2°F (−21 ± 1°C) for 1 h, and then a return to room temperature for 30 min. The number of cycles used is a decision by the testing agency.

FLAME RETARDANCE

Terminology

The technical terminology relating to flame retardance must be understood. The general concept concerned is *burning characteristics*. (With one exception [*1*], these standard definitions are found in ASTM Terminology of Fire Standards (E 176). Several interrelated terms are:

- *fire performance test*—A procedure that measures the response of a material, product, or assembly to heat or flame under controlled conditions. A fire performance test allows the quantitative description of one or more fire performance characteristics for the specific fire and other parameters of the test.
- *fire resistance*—The property of a material or an assemblage to withstand fire or to provide protection from it.
- *fire retardancy*—In paint, this is the ability of a paint to retard the spread of flame over a coated substrate, usually at the sacrifice of the paint film.
- *fire-retardant coating*—A fluid-applied surface covering on a combustible material that delays ignition and combustion of the material when the coating is exposed to fire.
- *flame resistance*—The ability to withstand flame impingement or give protection from it.
- *flame-retardant coating*—A fluid-applied surface covering on a combustible material which delays ignition and re-

[1]Deceased, formerly of Harleysville, PA.

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duces flame spread when the covering is exposed to flame impingement.

- *flame-spread index*—A number or classification indicating a comparative measure derived from observations made during the progress of the boundary of a zone of flame under defined test conditions.
- *surface flame spread*—The propagation of a flame away from the source of ignition across the surface of a liquid or a solid.

Rationale for Test Selection

Note the conceptual difference in the definitions between fire-retardant and flame-retardant coating. Testing coatings for burning characteristics may be carried out to compare the response to flame exposure of different specimens or to evaluate the performance under fire conditions. In the former mode, small-scale testing is appropriate. But, while small-scale testing may be useful in preliminary evaluations in the latter mode, large-scale testing is essential if test results are to be used as a measure of performance in fires in buildings or other structures. Small-scale tests are categorized as flame-test standards. Large-scale tests are categorized as fire-test-response standards. Only the latter are appropriate in fire risk assessments. The scale of test is indicated in each of the following test method descriptions.

Tests for Combustibility

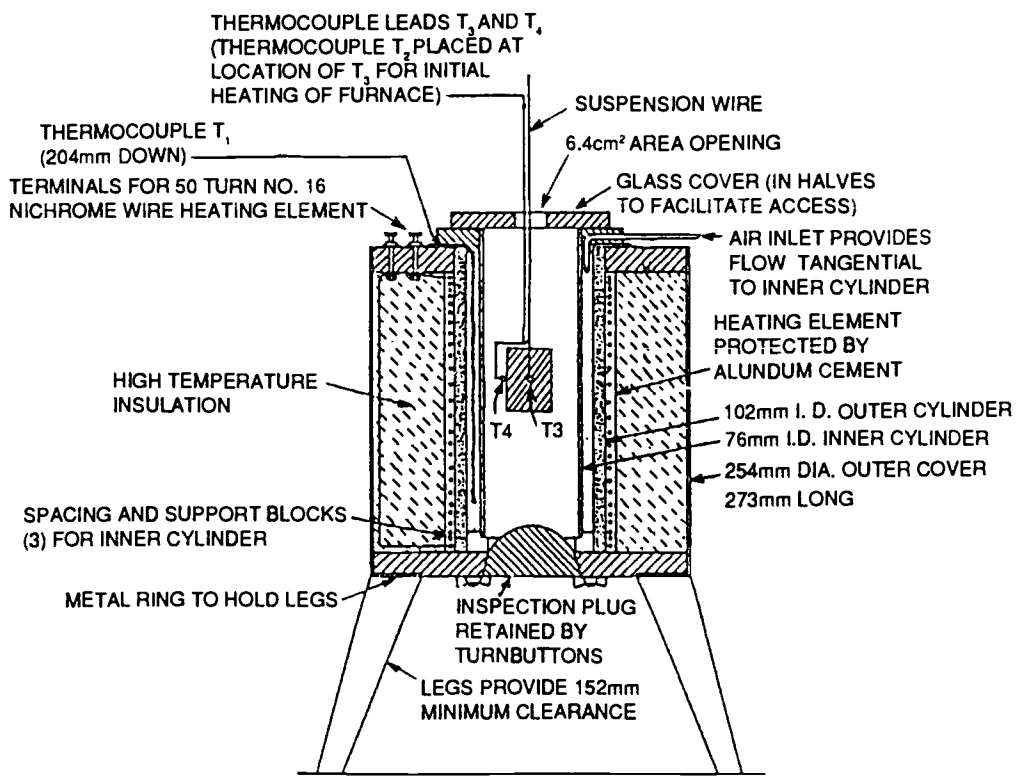
ASTM Method E 136

ASTM Test Method for Behavior of Materials in a Vertical Tube Furnace at 750°C (E 136) is a small-scale method designed to identify materials that do not aid combustion or add appreciable heat to an ambient fire. This method is not intended to apply to laminated or coated materials; however, it is useful in evaluating material believed not to be combustible.

Figure 1 shows a cross section of the vertical tube furnace. The specimen, nominally 1.5 in. (38 mm) wide by 1.5 in. (38 mm) thick in cross section with thermocouples attached, is inserted in a furnace controlled at 1382 ± 10°F (750 ± 5.5°C) and held there until temperatures at the specimen thermocouples are at furnace temperature. The standard contains an instructive commentary section describing the rationale for the test, its limitations, and usefulness of the test results. This test method presently does not contain a precision and bias statement.

ASTM Method D 2863

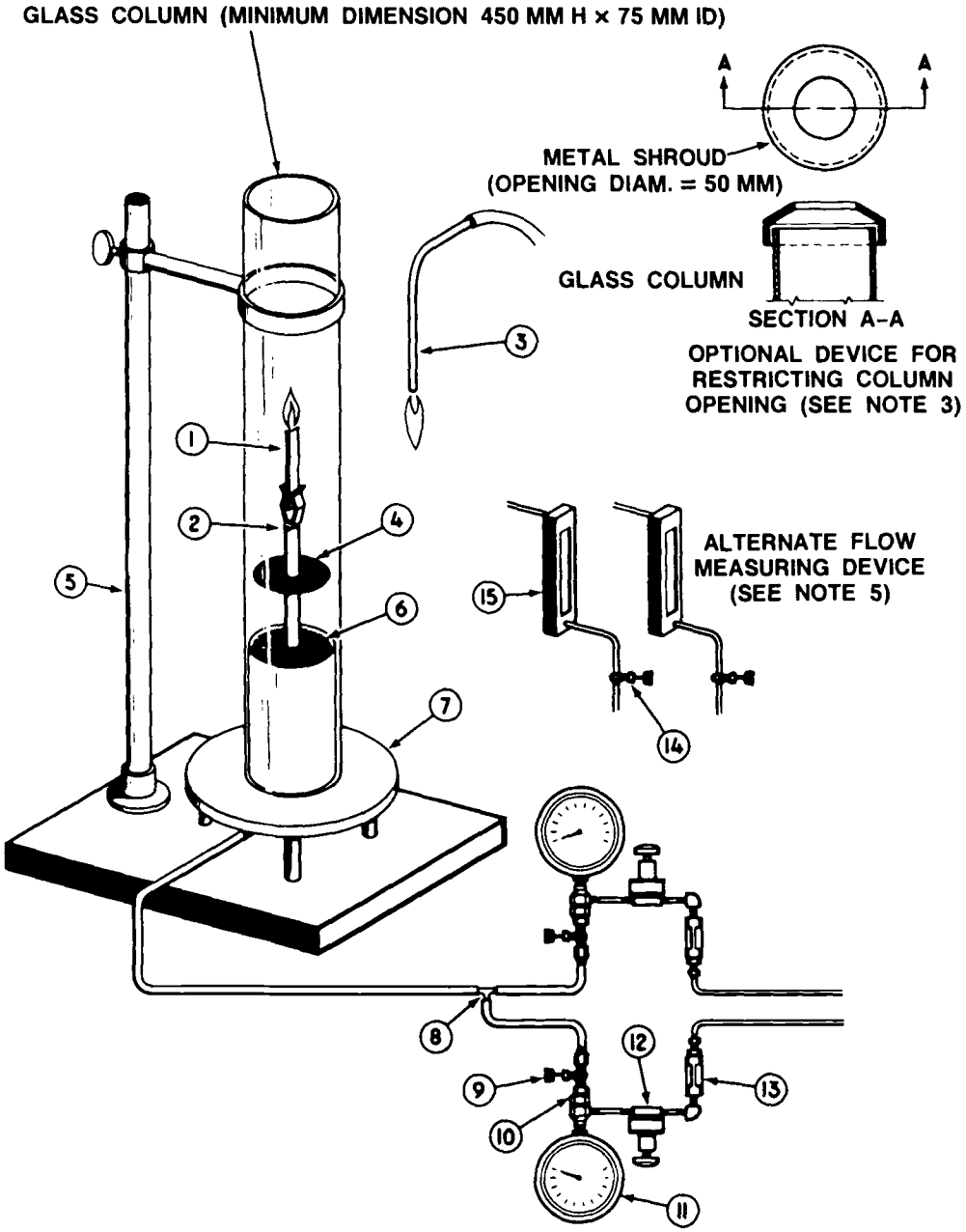
ASTM Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-like Combustion of Plastics (Oxygen Index) (D 2863) is a small-scale method that measures the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that will just support flaming combustion. Figure 2 shows the typical equipment layout. Film or thin-sheet test specimens are nominally 2.0 in (52



Inch-Pound Equivalents

mm	76	102	152	254	273	6.4 cm²	1.29
in.	3	4	6	10	10¾	1 in.²	No. 16 Awg

FIG. 1–Cross section of furnace assembly.



1. Burning Specimen
2. Clamp with Rod Support
3. Igniter
4. Wire Screen
5. Ring Stand
6. Glass Beads in a Bed
7. Brass Base
8. Tee
9. Cut-Off Valve
10. Orifice in Holder
11. Pressure Gage
12. Precision Pressure Regulator
13. Filter
14. Needle Valve
15. Rotameter

FIG. 2–Typical equipment layout.

mm) wide and 5.5 in. (140 mm) long. The minimum oxygen concentration is measured under equilibrium conditions of candle-like burning. The equilibrium is established by the relation between the heat generated from the combustion of the specimen and the heat lost to the surroundings as measured by one or the other of two arbitrary criteria, namely, a time of burning or a length of specimen burned. This point is approached from both sides of the critical oxygen concentration to establish the oxygen index.

While this method is useful for comparing resistance to combustion of organic materials, correlation with burning characteristics under actual use conditions is not implied. *Precision*: In a testing program in which 18 laboratories checked the same five materials, the standard deviation was 0.4 for materials with an oxygen index below 21% and 0.7 to 1.4 for materials with an oxygen index above 21%. Table 1 contains results from another test series. *Bias*: There are no recognized standards on which to base an estimate of bias.

ASTM Method D 1360

ASTM Test Method for Fire Retardancy of Paints (Cabinet Method) D 1360 is a small-scale test method. This procedure measures the relative fire-retardant properties of coatings by determining the weight loss and char index of coated wood panels exposed to flaming ethyl alcohol. It is useful for comparing the burning behavior of coating materials under specified conditions; however, the test results do not always correlate with large-scale spread-of-flame tests, such as ASTM Test Method for Surface Burning Characteristics of Building Materials (E 84). D 1360 is a measure of combustibility, through weight loss, rather than a measure of flame-spread index value. The precision of this method is yet to be determined.

Tests for Flame Spread

ASTM Method D 3806

ASTM Test Method for Small-Scale Evaluation of Fire-Retardant Paints (2-ft Tunnel Method) (D 3806) determines the protection afforded to a substrate by a coating by evaluating the flame spread over the coated surface when the specimen is ignited under controlled conditions in a small tunnel. Figure 3 shows the layout of the 2-ft (610 mm) tunnel apparatus. The test panels are wood, ¼ by 3⅞ by 23⅞ in. (6 by 100 by 605 mm). The tunnel apparatus is calibrated with a zero-flame-spread panel and with another reference panel coated with a paint rated for flame spread by the method of ASTM E 84. A standard gas flame is applied to the lower end of the inclined test panel, and the progress of the flame front upward is observed, measured, and recorded at 15-s intervals. The test results establish a basis for comparing surface-burning characteristics of different coatings without specific consideration of all the end-use parameters that might affect surface-burning characteristics under actual fire conditions.

TABLE 1—Precision results.

Type	Laboratory-To-Laboratory Standard Deviation	Within Laboratory Standard Deviation
B	0.5 to 1.1	Below 0.2
C	0.4 to 1.5	0.1 to 0.3 (est.)
D	0.5 to 1.4	Below 0.6

The method is useful in laboratory comparison of intumescent paint formulations, but large-scale testing by Method E 84 is desirable for correlation with real fire conditions. *Precision*: Table 2 indicates the repeatability of this method. The standard deviation shown relates to the maximum difference that would be expected between duplicate specimens. The degree of repeatability is dependent on the level of flame-spread ratings.

ASTM Method E 162

ASTM Test Method for Surface Flammability of Materials Using a Radiant Heat Energy Source (E 162) is a small-scale procedure, intended for research and development purposes, for measuring the surface spread of flame under exposure to a radiant heat source. Figure 4 shows details of the test equipment. The specimen, which is representative of the material or assembly being evaluated, has dimensions of 6 by 18 in. (150 by 460 mm) by the sheet thickness. It is placed at a downward angle of 30° from the vertical, facing a gas-fired porous refractory heat-radiating surface, 12 by 18 in. (300 by 460 mm), operating at 1238°F (670°C). The rate at which flames travel along the surface depends on the physical and thermal properties of the specimen. The orientation of the specimen is such that ignition is forced near its upper edge and the flame front progresses downward. The time of arrival of the flame front at each of 3-in. (76-mm) marks on the specimen holder is recorded, and observations are made for flashing, dripping, and any other behavior characteristics that appear to be of interest. The maximum temperature rise as indicated by thermocouples in the stack is recorded. The test is completed when the flame front has progressed to the 15-in. (380-mm) mark or after an exposure of 15 min, whichever occurs first, provided the maximum temperature of the stack thermocouples is reached.

A flame-spread index, I_s, is calculated as the product of the flame-spread factor, F_s, and the heat evolution factor, Q. F_s is calculated from a plot of

$$I_s = F_s Q$$

with vertical distance as a function of flame-arrival time at each horizontal mark. The Q factor is calculated from the equation $Q = CT/\beta$, where C is an arbitrary constant, T is the observed maximum stack-thermocouple temperature difference between the temperature-time curve for the specimen and that for a similar curve of a calibration specimen, and β is the mean stack thermocouple rise for unit heat input of a calibration burner. The flame-spread indices determined by this method may be compared with those determined in ASTM Method E 84, although correlation is not necessarily obtained. A precision and bias statement for this method is being developed by ASTM Committee E-5 on Fire Standards.

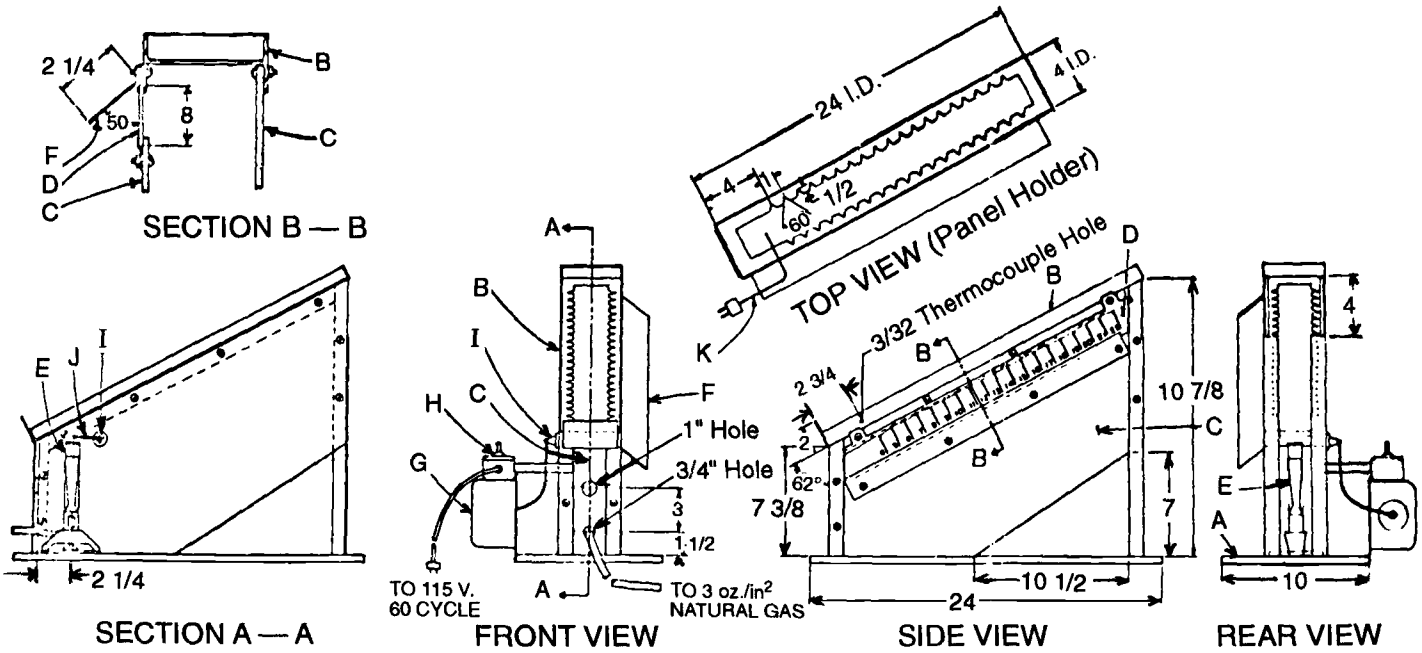
ASTM Method E 84

ASTM Test Method for Surface Burning Characteristics of Building Materials (E 84) is also called the 25-ft (7.6-m) tunnel test, or the Steiner tunnel test, or the NFPA 255 test. A large-scale test, E 84 is applicable to exposed finishes on ceilings or walls. The test is conducted with the material in a horizontal position with the exposed surface facing downward. The purpose of the test is to determine the relative

Materials of Construction and Equipment List

Item No	Item	Description	Item No	Item	Description
A	Base Plate	½ × 10 × 24 Steel plate	F	Glare Shield	1/16 × 2¼ × 22 Metal sheeting
B	Framework	⅛ × 1 × Angle iron throughout	G	Ignition Transformer	115 V, 60 Hz, 5000 V, 20 A secondary
C	Side and Front Panels	¼ Transite cut to specifications	H	Spark Switch	Push button type
D	Side Glass	⅛ × 2 × 24 Polished Vycor cut as shown	I	Ceramic Insulator	
E	Burner	Artificial Gas Model	J	Spark Wire	1/16 OD Nichrome
	Gas Control Valve (not shown)	⅛ Orifice, 1″ Pipe size, outlet 3 oz/in^2	K	Thermocouple	Megopak Type J, totally shielded
	Gage, Gas (not shown)	0–30 oz/in^2 Dial		Recording Potentiometer	115 V, 60 Hz, 0–300°C, Type J concl

Note: All Dimensions Expressed in Inches Unless Otherwise Noted.



METRIC EQUIVALENTS

in.	mm	in.	mm
1/16	1.6	3	76
3/32	2.4	4	102
⅛	3.2	7	178
¼	6.4	7⅜	187
½	12.7	10	254
1	25.4	10½	267
1½	38	18⅝	480
2¼	57	22	560
2¾	70	24	610

FIG. 3–Flame tunnel.

TABLE 2—Repeatability.[a]

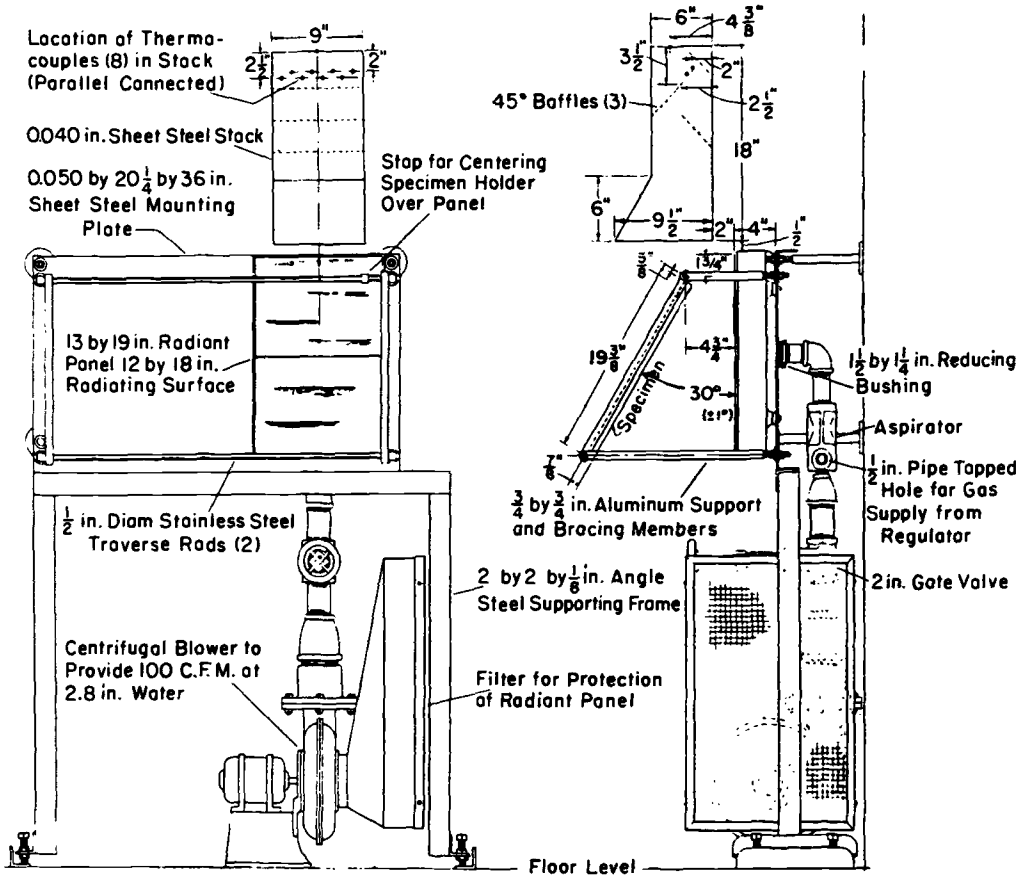
Flame-Spread Ratings	Standard Deviation	Coefficient of Variation
0 to 25	1.2	9.6
25 to 75	3.1	6.2
75 to 135	3.65	3.5
0 to 135	2.85	4.6

[a]This information was derived from *Journal of Paint Technology*, Vol. 39, No. 511, 1967, p. 495.

burning behavior of the specimen by observing flame spread. The test exposes a nominal 24-ft (7.32-m)-long by 20-in. (508-mm)-wide specimen to a controlled air flow and flaming fire exposure adjusted to spread the flame along the entire length of a reference material (select-grade red oak) in 5.5 min. A photoelectric cell is placed at the vent end to detect and record smoke emission. Figure 5 shows details of the test furnace and the specimen placement.

The specimen is exposed to the standard flame conditions for 10 min or less if the specimen is completely consumed in the fire area and no further progressive burning is evident and if the photoelectric cell reading has returned to the baseline. The flame-spread index (FSI) is determined by calculation from the plotted time-distance curve in relationship to the area under a similar curve for the reference material, select grade red oak. Arbitrarily, red oak is assigned a flame-spread index of 100 and the inorganic reinforced-cement board an FSI rating of zero. The precision and bias of this method has yet to be determined.

Several studies have been conducted to examine the relationship of the flame-spread index (FSI) test results obtained for materials with their behavior in large-scale fire-growth

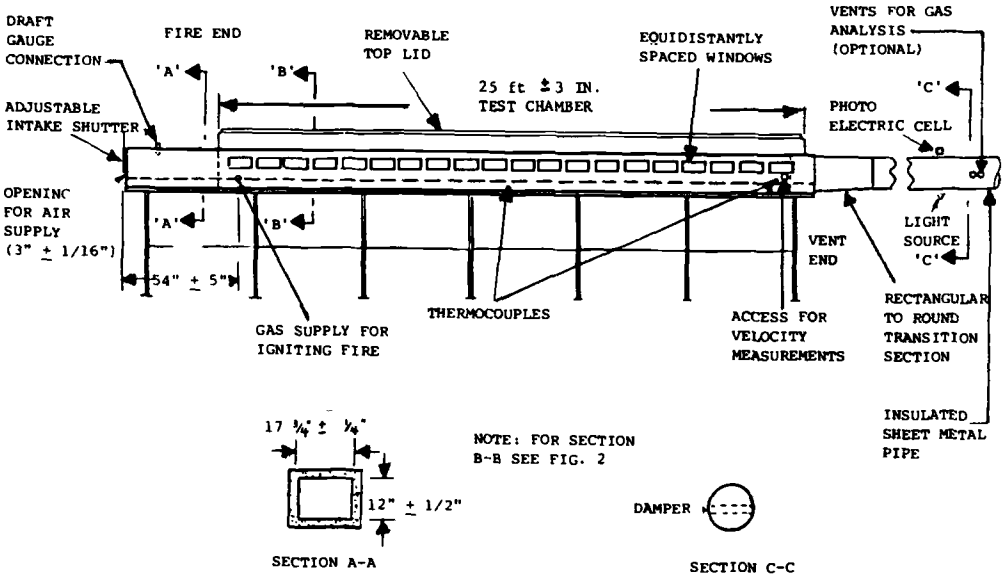


Metric Equivalents

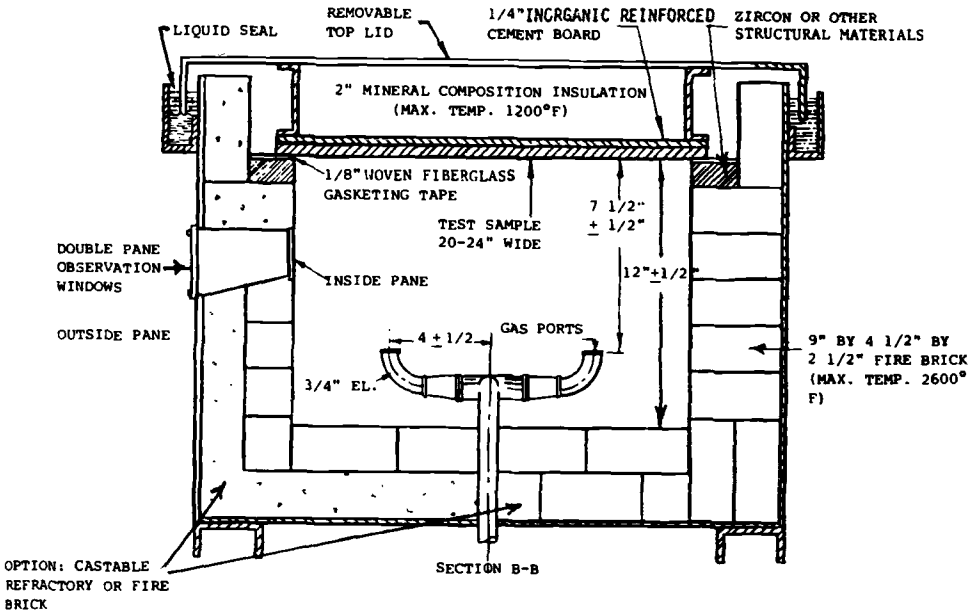
in.	mm	in.	mm
0.040	1.0	6	152
½	12.7	9½	241
⅝	16.0	18	457
⅞	22.2	19⅜	492
1¾	44	¾ by ¾	19.2 by 19.2
2	51	1½ by 1¼	38 by 32
2½	64	12 by 18	305 by 457
2.8	71	13 by 19	330 by 483
4	102	2 by 2 by ⅛	51 by 51 by 3.2
4⅜	111	0.050 by 20¼ by 36	13 by 514 by 914
4¾	121		

100 ft³/min = 47.21 L/s

FIG. 4—Details of construction of test equipment.



Inch-Pound Units	SI Units
12 ± ½ in.	305 ± 12.7 mm
17¾ ± ¼ in.	451 ± 6.3 mm
54 ± 5 in.	1371 ± 127 mm
25 ft	7.62 m



Inch-Pound Units	SI Units	Inch-Pound Units	SI Units
¼ in.	6.3 mm	20 in.	508 mm
2 in.	51 mm	9 by 4½ by 2½ in.	230 by 115 by 65 mm
4 ± ½ in.	102 ± 13 mm	1200°F	649°C
7½ ± ½ in.	191 ± 13 mm	2600°F	1427°C
12 ± ½ in.	305 ± 13 mm		

FIG. 5–(top) Test furnace, showing some critical dimensions (not a construction drawing); (bottom) test furnace showing some critical dimensions (Section "B-B" is not a construction drawing).

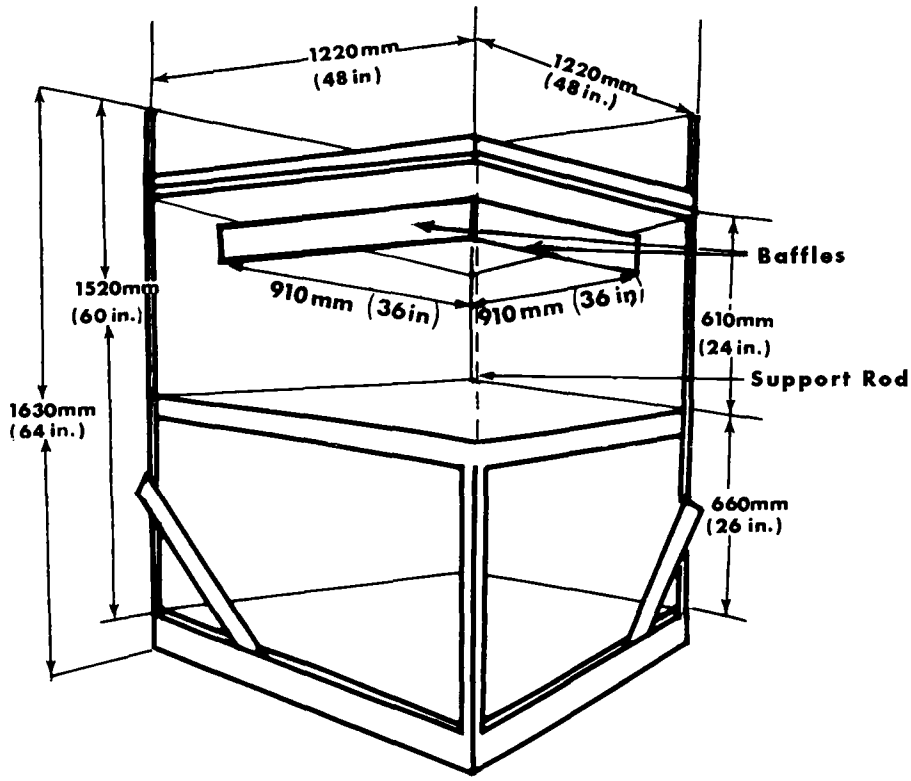


FIG. 6–Corner construction.

experiments and with the fire-test response of other laboratory methods. Reports of other comparisons with large-scale experiments can be found in the references to this chapter. Comparisons have also been made between Test Methods E 84, E 162, and D 3894 [*1*].

ASTM Method D 3894

ASTM Test Method for Evaluation of Fire Response of Rigid Cellular Plastics Using a Small Corner Configuration (D 3894) is intended for evaluation of cellular plastics; however, this large-scale test is useful for characterization of the burning behavior of coatings applied to representative substrates. It simulates configurations of two adjacent walls or two adjacent walls and ceiling. It is useful in predicting performance of such materials in a Factory Mutual Laboratories full-scale corner wall test.[2] Figure 6 shows the corner construction of the D 3894 setup. The test configuration provides a critical surface geometry affording a combined heat flux that includes the conductive, convective, and radiative responses of any specific burning material.

The specimen consists of a corner, supported by an outside frame, made from panels each measuring 610 by 1220 by *T* mm (2 by 4 ft by *T* in.), *T* being the thickness of the test panel, and a ceiling section of similar composition measuring 1220 by 1220 by *T* mm (4 by 4 ft by *T* in.). A standard burner is used for ignition. Visual observations are made, and a record of flame-travel distance from the test corner junction outward on the horizontal plane is made at the start of the test and at least every 15 s for the test duration. The test is terminated after 20 min or sooner if the flame becomes uncontrollable. *Precision*: Tables 3 and 4 are based on a round robin involving five materials tested by five laboratories. *Bias*: There are no recognized standards by which to estimate bias of this test method.

[2]For details contact Factory Mutual Research Corp., P.O. Box 09102, Norwood, MA 02062.

Full-Scale Compartment Fire Tests

ASTM Method E 603

At present there is no ASTM standard test method for conducting full-scale room fire tests, although there is considerable experimental activity. ASTM Guide for Room Fire Experiments (E 603) describes full-scale compartment fire experiments designed to evaluate the fire characteristics of materials, products, or systems under actual fire conditions. E 603 is intended as a guide for design of experiments and for the interpretation of the results. The guide may be used to establish laboratory conditions that simulate a given set of fire conditions as realistically as possible.

TABLE 3—Precision for maximum flame spread for polyisocyanurate cellular plastic, glass-fiber-filled, 1-in. thick, covered with aluminum foil.

	Average, in.	Values Expressed as Percent of the Average			
		ν_r[a]	ν_R[b]	l_r[c]	l_R[d]
Walls and ceiling	34	5	13	14	37
Walls only	27	21	32	59	91

[a]ν_r is the within-laboratory coefficient of variation of the average.
[b]ν_R is the between-laboratories coefficient of variation of the average.
[c]$l_r = 2.83\ \nu_r$.
[d]$l_R = 2.83\ \nu_R$.

TABLE 4—Precision for time to maximum flame travel.

	Average, min	Values Expressed as Percent of the Average			
		v_r[a]	v_R[b]	l_r[c]	l_R[d]
Walls and Ceiling:					
Material: 4	0.46	12	26	34	74
5	0.56	26	35	74	99
3	1.02	26	58	74	164
1	4.76	18	19	51	54
2	8.51	8	12	23	34
Walls Only:					
Material: 4	1.34	12	49	34	139
5	2.28	91	95	257	269
3	6.88	10	50	28	141
1	7.39	15	28	42	79
2	9.14	12	15	34	42

Materials:

4 = Rigid polyurethane cellular plastic, 25.4 mm (1 in.), w/FR > 25 FS.
5 = Rigid polyurethane cellular plastic, 25.4 mm (1 in.), 2 pcf.
3 = Rigid isocyanurate cellular plastic, 25.4 mm (1 in.), 2 pcf.
1 = Plywood, ½ in. AD.
2 = Same as in Table 3.

[a] v_r is the within-laboratory coefficient of variation of the average.
[b] v_R is the between-laboratories coefficient of variation of the average.
[c] $l_r = 2.83\ v_r$.
[d] $l_R = 2.83\ v_R$.

Analysis of data from room fire experiments can serve two purposes: (1) to relate the severity of the room fire experiment to the laboratory-measured fire properties, which establishes empirical relationships that validate the strengths and the weaknesses of the various fire test methods now being used or proposed to control the materials to be used in the rooms; and (2) to evaluate materials and products for acceptability, particularly those materials for which there are no adequate material property tests. This standard contains a detailed rationale for full-scale compartment fire tests. It should be consulted in detail.

Testing Intumescent, Fire-Retardant, and Ablative Coatings

These special-purpose coatings are intended to protect substrates from damage by fire exposure. Intumescent coatings are designed for cellulosic substrates, as fire-retardant coatings for structural steel substrates, and as ablative coatings for the exterior of re-entry space vehicles. See the reference section for more specific references.

Intumescent coatings applied to wood panels are tested for flame-spread index by ASTM E 84. Evaluation of fire-retardant coatings for the protection of structural steel is conducted according to ASTM E 119.

ASTM Method E 119

ASTM Method for Fire Tests of Building Construction and Materials (E 119) is a large-scale fire endurance test applicable to assemblies of masonry units and to composite assemblies of structural materials for buildings, including load-bearing walls and other walls, partitions, columns, girders, beams, slabs, and composite beam and slab assemblies for floors and roofs. It is also applicable to other assemblies and structural units that constitute permanent and integral parts of a finished building.

E 119 is the principal method for evaluating structural integrity of building assemblies under actual fire conditions. It is the method designated in building codes and fire codes to rate structural integrity in fire exposure. The test exposes a full-scale specimen within a standard furnace to a standard fire that is controlled to achieve specified temperatures throughout a prescribed time period. The test measures heat transmission and measurement of load-carrying ability of the specimen during the test exposure. Figure 7 is the time-temperature relationship used in controlling the test. Precision and bias of the method are not stated. Method E 119 has been in wide and continuous use since 1917 for fire rating building assemblies. It has wide acceptance.

There are no standard test methods for ablative coatings. NASA SP 5014 [2] describes the general topic. Thermogravimetric analysis is useful in understanding the effect of high temperature on inorganic as well as organic coatings.

ASTM Method E 1131

ASTM Test Method for Compositional Analysis by Thermogravimetry (E 1131) provides a general technique incorporating thermogravimetry to determine amounts of volatile matter, combustible material, and ash content of compounds. It is applicable, using either an inert or a reactive gas environment, to solids and liquids in the temperature range from room temperature to 1830°F (1000°C). The test method is an empirical technique using thermogravimetry in which the mass of a substance, heated at a controlled rate in an appropriate environment, is recorded as a function of time or temperature.

Historical Methods

The heat and fire test methods described are those most used today in characterizing coatings. Historically, a variety of other bench-scale screening tests have been used, but they are no longer in vogue as they do not relate to actual service

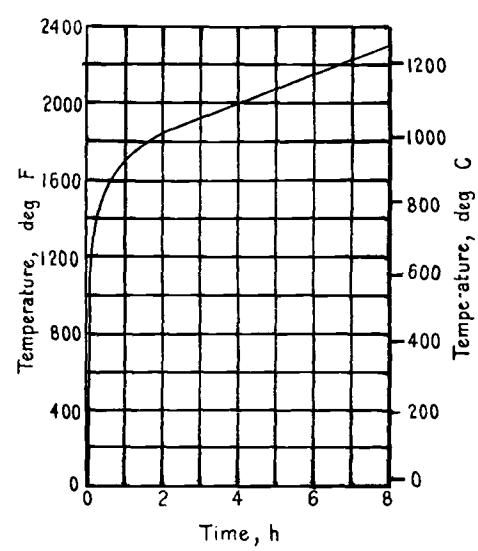


FIG. 7—Time-temperature relationship used for test control.

conditions. Details of the following historical tests may be found in ASTM STP 500 [*3*]: Schulz fire-retardant tester, NJZ box test, stick and wick test, vertical match test, crib test, fire-tube test, SS-A-118 acoustical tile test, Schlyter test, and the 8-ft tunnel test.

Recommendations for Further Reading

Additional background material can be found in Refs *4-7*.

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[*1*] McGuire, J. H., "The Spread of Fire in Corridors," *Fire Technology*, Vol. 4, No. 2, May 1968, pp. 103-108.

[*2*] Plunkett, J. D., "NASA Contributions to the Technology of Inorganic Coatings," NASA SP-5014, 1964.

[*3*] Van Heuckeroth, A. W., "Fire Retardance and Heat Resistance," Chap. 6.3, *Paint Testing Manual*, 13th ed., American Society for Testing and Materials, Philadelphia,1972, pp. 355–365.

[*4*] Babrauskas, V. and Williamson, R. B., "Historical Basis of Fire Resistance Testing," *Fire Technology*, Vol. 14, Nos. 3 and 4, 1978, pp. 184–198, 304–316.

[*5*] Magee, R. S. and McAlevy, R. F., III, "The Mechanism of Flame Spread," *Journal of Fire and Flammability*, Vol. 2, 1971, pp. 271–297.

[*6*] Shorter, G. W., Ed., *Fire Test Performance, ASTM STP 464*, p. 1070.

[*7*] Williamson, R. B. and Baron, F. M., "A Corner Test to Simulate Residential Fires," *Journal of Fire and Flammability*, Vol. 4, April 1973, pp. 91–105.

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Water-Resistance Testing of Coatings

*by Wayne Ellis**

OTHER CHAPTERS IN THIS MANUAL cover the influence of water on the formulation and durability of organic coatings. Recent ASTM publications about the moisture effects in building materials are listed in the Bibliography at the end of this chapter. These publications describe moisture problems and solutions involving coatings and their uses. Although this chapter is intended to describe only the principal testing and evaluation of water resistance, some general remarks may be helpful in understanding the test conditions.

EFFECTS ON COATINGS OF EXPOSURE TO WATER AND WATER VAPOR

The adhesion of coatings to substrates is strongly influenced by the absorption of water and by the permeability of the coating to water vapor. The mechanism of this influence proceeds as follows:[1]

1. Absorption of water molecules in the coating film.
2. Inclusion of water in the interface between film and substrate.
3. Blister formation.
4. Corrosion/erosion of the substrate.
5. Flaking or peeling of the film.

Although there is no fixed relationship between water absorption and water vapor permeability, generally the higher the water absorption the more permeable the film is to water vapor. Normally the permeability measurements are made on freshly applied films. It should be noted that with progressive aging and weathering, films become more cross-linked, and in the case of water-sensitive binders, the water-soluble additives are washed out by exposure to rain and dew. Hence such films will show decreasing permeability with time.

Water resistance is defined by ASTM as "measured ability to retard both penetration and wetting by water in liquid form".[2] Nearly always it is a required property for coatings. Water resistance generally is measured on specimens of coatings applied to nominally impermeable substrates such as metal, wood, or masonry. (Water vapor permeability, on the other hand, is evaluated on free films.) Water resistance may be evaluated as part of other test regimes, such as exposure testing, water repellency, corrosion, chemical resistance, salt-fog resistance, and cycling tests such as humidity-cycling and light-and-water-exposure testing.

TRADITIONAL TEST METHODS

Spot tests and immersion tests of coatings applied to substrates traditionally have been used as "quick and dirty" techniques to compare specimens. Criteria for evaluation include softening, blistering, solvation, color change, loss of adhesion, and rusting or other deterioration of the substrate. These observations should lead to further and more comprehensive testing related to intended conditions of product use. Such testing may include exposure to controlled condensation, 100% relative humidity, or water fog to evaluate moisture blistering resistance. Even more intensive testing may involve washability and scrub resistance.

SPECIMEN PREPARATION

Careful preparation of coated specimens is essential to assure a proper and meaningful relationship to field exposure and to avoid false test results. The substrate composition and surface preparation, specimen preparation, and the number of specimens should be agreed upon between involved parties prior to testing. Applicable methods for the preparation of test panels are given in ASTM Methods D 609,[3] D 1734,[4] and Practices D 1730.[5] Test Methods D 823[6] cover application techniques for the production of uniform films.

IMMERSION TESTING

ASTM Practice for Testing Water Resistance of Coatings Using Water Immersion (D 870) describes basic principles

*Wayne Ellis is deceased. He was a former Chairman of the Board of ASTM and served as a standards consultant and First Chairman of the Board of the Building Environment and Thermal Envelope Council.

[1]Eric V. Schmid, *Exterior Durability of Organic Coatings*, Redhill, Surrey: FMJ International Publications, 1988.

[2]ASTM D 996, Terminology of Packaging and Distribution Environment.

[3]D 609, Practice for Preparation of Cold-Rolled Steel Panels for Testing Paint, Varnish, Conversion Coatings, and Related Coating Products.

[4]D 1734, Method of Making and Preparing Concrete and Masonry Panels for Testing Paint Finishes.

[5]D 1730, Practices for Preparation of Aluminum and Aluminum-Alloy Surfaces for Painting.

[6]D 823, Test Methods for Producing Films of Uniform Thickness of Paint, Varnish, and Related Products on Test Panels.

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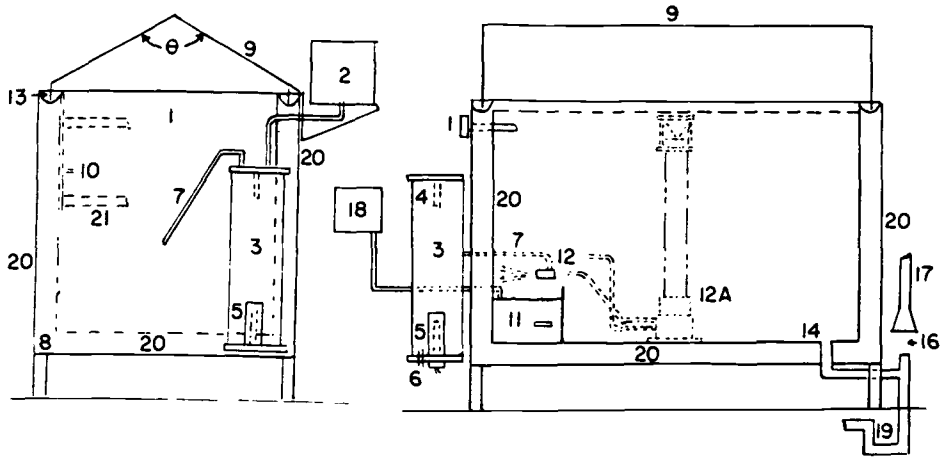


θ—Angle of lid, 90 to 125°
1—Thermometer and thermostat for controlling heater (Item No. 8) in base
2—Automatic water levelling device
3—Humidifying tower
4—Automatic temperature regulator for controlling heater (Item No. 5)
5—Immersion heater, nonrusting
6—Air inlet, multiple openings
7—Air tube to spray nozzle
8—Strip heater in base
9—Hinged top, hydraulically operated, or counterbalanced
10—Brackets for rods supporting specimens, or test table
11—Internal reservoir
12—Spray nozzle above reservoir, suitably designed, located, and baffled
12A—Spray nozzle housed in dispersion tower located preferably in center of cabinet
13—Water seal
14—Combination drain and exhaust. Exhaust at opposite side of test space from spray nozzle (Item 12), but preferably in combination with drain, waste trap, and forced draft waste pipe (Items 16, 17, and 19).
16—Complete separation between forced draft waste pipe (Item 17) and combination drain and exhaust (Items 14 and 19) to avoid undesirable suction or back pressure.
17—Forced draft waste pipe
18—Automatic levelling device for reservoir
19—Waste trap
20—Air space or water jacket
21—Test table or rack, well below roof area

FIG. 1–Typical salt spray cabinet (Fig. X1.1 of ASTM B 117).

and operating procedures for testing water resistance of coatings by the partial or complete immersion of coated specimens in distilled or demineralized water at ambient or elevated temperatures. Coated specimens are partly or wholly immersed in water in a container that is resistant to corrosion. The exposure conditions are varied by selecting the temperature of the water and the duration of the test.

Failure may be caused by a number of factors, including a deficiency in the coating itself, contamination of the substrate, or inadequate surface preparation. Any effects such as color change, blistering, loss of adhesion, softening, or embrittlement are observed and reported. These test results typically are a pass or fail determination, but the degree of failure also may be measured.

WATER FOG TESTING

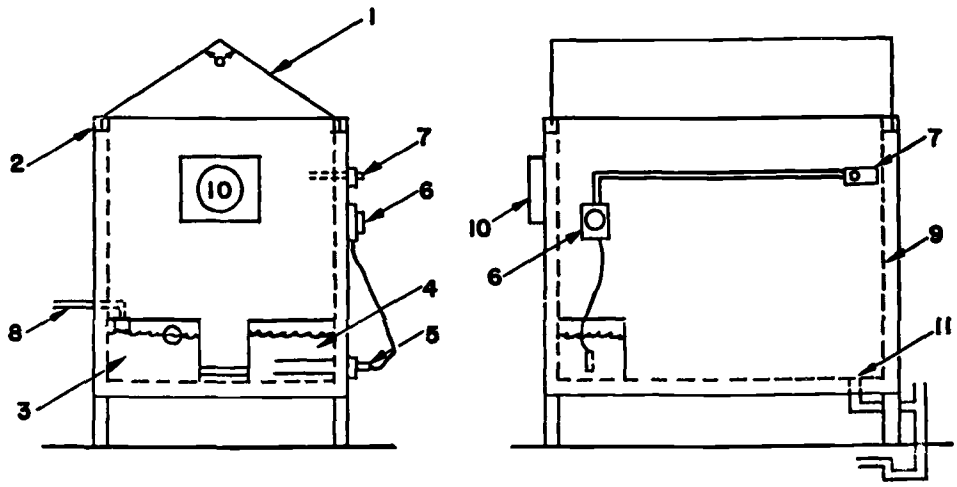
ASTM Practice for Testing Water Resistance of Coatings Using Water Fog Apparatus (D 1735) covers the basic principles and operating procedures for testing water resistance of coatings in an apparatus similar to that used for salt spray testing.[7] The apparatus required consists of a fog chamber (Fig. 1), a water reservoir, a supply of suitably conditioned compressed air, one or more atomizing nozzles, specimen supports, provision for heating the chamber, and necessary means of control. Coated specimens are placed in an enclosed chamber where a water fog surrounds them. The temperature of the chamber is usually maintained at 100°F (38°C). The exposure condition is varied by selecting the duration of the test.

Failure in water fog tests may be caused by a number of factors, including a deficiency in the coating itself, contamination of the substrate, or inadequate surface preparation. Any effects such as softening (measured by pencil hardness), color change, gloss change, blisters, loss of adhesion, embrittlement, and rusting or corrosion of substrate are observed and reported.

100% RELATIVE HUMIDITY TESTING

Practice for Testing Water Resistance of Coatings in 100% Relative Humidity (D 2247) covers the basic principles and operating procedures for testing water resistance of coatings by exposing coated specimens in an atmosphere maintained at 100% relative humidity so that condensation forms on the

[7]ASTM B 117, Test Method of Salt Spray (Fog) Testing.



0—Angle of lid, 90 to 125°
1—Hinged top, hydraulically operated, or counterbalanced
2—Water seal
3—Constant-level water tank unheated with overflow outlet and equalizer connection
4—Heater water tank for supplying heat and humidity to cabinet
5—Immersion heater
6—Water temperature limit control
7—Thermostatic controller for room temperature. Primary limit control for immersion heater (5)
8—Water line
9—Insulation if necessary (see A1.3)
10—Temperature recorder (optional)
11—Drain

FIG. 2–Humidity cabinet (Fig. A1.1 of ASTM D 2247).

specimens. The apparatus (Fig. 2) consists of a test chamber, a heated water tank, and suitable controls. Heated water vapor is generated at the bottom of the chamber, causing saturation of the air immediately above the water tank. As the saturated mixture rises, it cools below the dew point temperature, causing condensation on the specimens suspended above. Condensation is uncontrolled. (For testing at 100% RH with controlled condensation, see ASTM D 4585, described below.)

Effects of exposure at 100% relative humidity may be color change, blistering, loss of adhesion, softening, or embrittlement. Any such effects are observed and reported. They may be caused by a number of factors including a deficiency in the coating itself, contamination of the substrate, or inadequate surface preparation.

CONTROLLED CONDENSATION TESTING

Practice for Testing Water Resistance of Coatings Using Controlled Condensation (D 4585) differs from D 2247 in that the coated specimens are mounted with the uncoated face exposed to room temperature air. The apparatus (Figs. 3 and 4) consists of a test chamber in which the specimens form the roof of a chamber that is fitted with suitable water supply and controls.

Water vapor is generated by heating a pan of water at the bottom of the test chamber. The specimens form the roof or walls of the test chamber so that the back sides of the specimens are exposed to the cooling effects of room temperature air. The resulting heat transfer causes water vapor to condense on the coated specimens as liquid water saturated with

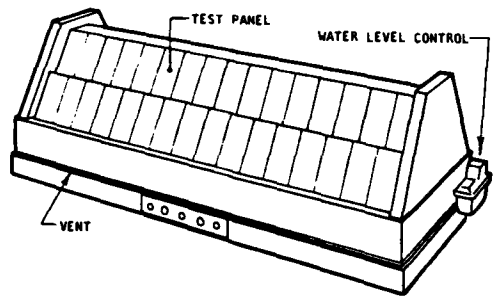


FIG. 3–Controlled condensation apparatus (Fig. 1 of ASTM D 4585).

air. The temperature and amount of condensate forming on the specimens are controlled by the test temperature and room temperature.

The specimens are inclined so that the condensate runs off the test surface by gravity and is replaced by fresh condensate in a continuous process during the condensate cycle. Exposure conditions are varied by selecting the temperature of the test, the duration of the test, and periodic drying of the specimens. Failure may be caused by a number of factors including a deficiency in the coating itself, contamination of the substrate, or inadequate surface preparation. Any effects such as color change, blistering, loss of adhesion, softening, or embrittlement are observed and reported.

CYCLE TESTING

Test Method for Finishes on Primed Metallic Substrates for Humidity-Thermal Cycle Cracking (D 2246) covers an accel-

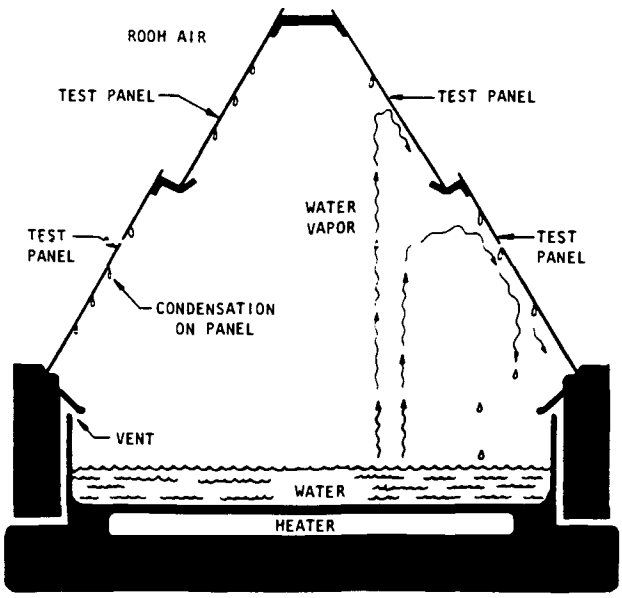


FIG. 4–Apparatus and cross section (Fig. 2 of ASTM D 4585).

erated means for determining the tendency of an organic coating to fail by cracking when exposed to humidity-thermal cycling. It is evaluated by alternate exposure of prepared specimens in a cabinet maintained at 100°F (38°C) and 100% relative humidity (with continuous condensation on the specimens), then in a cold box at −10°F (−23°C), allowing only a maximum of 30 s for transfer. Specimens are rated (using a grid overlay) by counting the number of grid squares within which one or more cracks is visible. Evaluation before and after exposure may be done for checking (D 660[8]), for cracking (D 661[9]), for erosion (D 662[10]), and sometimes for water beading (D 2921[11]).

ASTM Test Method for Humid-Dry Cycling for Coatings on Wood and Wood Products (D 3459) is a procedure for evaluation of coatings designed for use on interior wood and wood products by exposure alternately to low and high humidity at an elevated temperature. Test panels having a minimum area of 12 by 12 in. (300 by 300 mm) are exposed in 48-h cycles in exposure chambers maintained at 97 ± 2% relative humidity and 122 ± 3.5°F (50 ± 2°C); the other chamber maintained at 50 ± 5% relative humidity and 73.5 ± 3.5°F (23 ± 2°C). At each change of conditions during cycling, the panels are inspected under strong light for possible damage or change, which may be in the base material or in the coating.

Testing for the effect of water exposure combined with other exposures is not described in this chapter. Such testing includes light-and-water exposure apparatus using carbon-arc ultraviolet,[12] Xenon-arc,[13] and fluorescent UV.[14]

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[8]D 660, Method for Evaluating Degree of Checking of Exterior Paints.

[9]D 661, Method for Evaluating Degree of Cracking of Exterior Paints.

[10]D 662, Method for Evaluating Erosion of Exterior Paints.

[11]D 2921, Method for Qualitative Tests for the Presence of Water Repellents and Preservatives in Wood Products.

[12]ASTM D 5031, Practice for Testing Paints, Varnishes, Laquers, and Related Products Using Enclosed Carbon-Arc Light and Water Exposure Apparatus.

[13]ASTM G 26, Practice for Operating Light-Exposure Apparatus (Xenon-Arc Type) With and Without Water for Exposure of Nonmetallic Materials.

[14]ASTM D 4587, Practice for Conducting Tests on Paints and Related Coatings and Materials Using a Fluorescent UV-Condensation Light- and Water-Exposure Apparatus.

Part 13: Specific Product Testing

Aerospace and Aircraft Coatings

58

by Charles R. Hegedus,[1] Stephen J. Spadafora,[2] David F. Pulley,[2] Anthony T. Eng,[2] and Donald J. Hirst[2]

ORGANIC COATINGS ARE PRIMARILY applied to aircraft for environmental protection and appearance. Reference *1* concludes, "The rate controlling parameter for the corrosion of aircraft alloys, excluding the mechanical damage factor, is the degradation time of the protective coating system." This clearly indicates the importance of the coating system's durability and its ability to control corrosion and erosion. Relative to appearance, commercial aircraft benefit from the aesthetic characteristics of the coating system, while military aircraft rely on camouflage properties to minimize enemy detection and tracking during mission operations.

To meet operational requirements, aircraft coating systems traditionally consist of a primer and a topcoat. Primers inhibit corrosion of the substrate and enhance adhesion of subsequent topcoats, while topcoats are applied for appearance and to enhance overall durability of the coating system. Self-priming topcoats, which perform as both primer and topcoat in a single coating, have recently been introduced [*2,3*]. In addition, specialty coatings are strategically applied to perform various functions such as protection against rain erosion, chafing, immersion in fuel, and high temperature. References *4* through *6* provide more detail on the formulation and properties of aircraft coatings.

A number of factors affect the performance of aircraft coatings, including the substrate material, the aircraft's operational environment, and flight conditions. Aircraft structures and skins are manufactured from numerous metallic alloys and polymeric composites with a variety of pre-paint treatments, thus complicating the adhesion and corrosion inhibition characteristics of the coating system. Environmental conditions also can vary dramatically (arctic, tropical, marine, industrial, desert, etc.). Skin temperatures during flight can range from −54 to 177°C (−65 to 350°F) while ground conditions may be relatively benign or highly corrosive. Aircraft type and mission also play important roles in coating system performance. A commuter aircraft that hops from island to island in the tropics sees frequent pressurization and depressurization along with high temperature, humidity, and salt water. In contrast, a military tactical aircraft may fly far fewer hours but will experience extreme structural loads during flight conditions. These flight conditions place environmental and mechanical stresses on the aircraft coating system. Therefore, selection of appropriate test and evaluation procedures is an essential component for determining acceptable coatings for aircraft application.

[1]Lead Applications Chemist, Air Products and Chemicals, 7201 Hamilton Blvd., Allentown, PA 18195-1501.

[2]Chemical Engineers, Materials Engineer, and Materials Engineering Technician, respectively, Naval Air Warfare Center, Aircraft Division, Warminster, PA 18974-0591.

VISCOSITY

The viscosity of aircraft coating components, component mixtures, and raw materials is valuable to the formulator, manufacturer, and applicator for assessment of rheological characteristics. These characteristics affect paint application properties such as atomization, leveling, sagging, and brushability.

Cup Methods (Cup Viscometers)

In aircraft coating specifications and at application sites, Zahn and Ford cup viscometers are used for admixed paints because they are inexpensive, easy to use and maintain, and produce practical quantitative data. Although the stand-mounted, standard Ford cup is more accurate due to its stability, deeper capillary orifice, and larger volume, the dip-type Zahn cup is preferred since it is easiest to use and maintain. Zahn and Ford viscometers are described in ASTM Test Method for Viscosity by Dip-Type Viscosity Cups (D 4212) and ASTM Test Method for Viscosity of Paints, Varnishes, and Lacquers by Ford Viscosity Cups (D 1200), respectively.

Brookfield and Stormer Methods

Brookfield and Stormer viscometers are rotation-type viscometers described in ASTM Test Method for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield) Viscometer (D 2196) and ASTM Test Method for Consistency of Paints Using the Stormer Viscometer (D 562), respectively. The Brookfield viscometer, which measures absolute viscosities in centipoises (cP) using a rotating spindle, is particularly effective in determining viscosities of non-Newtonian fluids due to its ability to measure shear stress (that is, torque of rotating spindle) at various speeds and shear rates. Since the cup viscometers described above offer relative simplicity and ease of use, the Brookfield viscometer is not used at application sites. However, it is frequently used as a research tool to characterize the viscosities of polymeric resin materials and dispersions.

The Stormer or Krebs-Stormer viscometer uses a rotating paddle to measure relative viscosity expressed in Krebs units.

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It is designed to provide controlled, uniform, and relative data based on a paddle-stirring motion. This type of viscometer is rarely used in the laboratory or required in current specifications due to the ease of use and maintenance of cup methods and to the accuracy of the Brookfield method.

DENSITY

Wet coating density measurements provide a check on the theoretical density value and on the uniformity of the manufactured product. Determination of density by any convenient or suitable method in this Manual is acceptable; however, a weight-per-gallon cup is normally used due to the ease of use of this instrument.

FINENESS OF GRIND AND COARSE PARTICLES

Fineness of grind and presence of coarse particles are determined to assess the quality and uniformity of the pigment dispersion and coating finish. In order to produce a high gloss coating of good appearance, a paint should be free of coarse particles. However, the extremely low gloss requirements of some aircraft camouflage paints require relatively large particle sizes. Fineness of grind is determined by ASTM Test Method for Fineness of Dispersion of Pigment-Vehicle Systems (D 1210), commonly referred to as the Hegman scale. The coarse particle content is determined by the weight retained on a 325-mesh sieve as specified in ASTM Test Methods for Coarse Particles in Pigments, Pastes, and Paints (D 185).

SOLIDS AND VOLATILE CONCENTRATION/ CONTENT

General

Several analysis techniques are used to determine the total solids, pigment concentration, and volatile concentration of aircraft coatings. This information can be used as a check on the coating composition when compared to the theoretical value as determined from the formulation. It can also be used to determine the quality of an as-received product and its potential surface coverage per volume of paint. In addition, restrictions on the volatile organic compounds (VOC) content of coatings increase the importance of determining the volatile concentration, and methods to determine this value are continuously being developed and refined. The following methods are currently used to determine these compositional properties for aircraft coatings.

Total Solids Content

The total solids content of a coating, often referred to as its nonvolatile content, is a measure of the combined polymer and pigment content in a paint. It is typically represented as the weight fraction or percentage of these "solid" components relative to the as-received "wet" coating. For aircraft coatings, this is determined by subtracting the volatile fraction of the coating from the total to determine the nonvolatile content. The method specified in ASTM Test Method for Volatile Content of Coatings (D 2369) is used. A method that provides a volumetric assessment is ASTM Test Method for Volume Nonvolatile Matter in Clear or Pigmented Coatings (D 2697).

Pigment Concentration

Three methods are available to determine the pigment weight concentration within a coating: ASTM Test Method for Determination of Pigment Content of Solvent-Type Paints by High Speed Centrifuging (D 2698); ASTM Practice for Separation of Vehicle from Solvent-Reducible Paints (D 2372); and Federal Standard 141 Method 4021, Pigment Content (Ordinary Centrifuge). These methods use the fact that pigment particles, generally being more dense than the vehicle, will settle under centrifugal force. One distinction between these methods is the variation in rinsing solvent(s) used to separate the polymer from the pigment. Although each method utilizes a different solvent blend, it is common to deviate from the specified method by using solvents which are appropriate for the specific paint under analysis. All three methods result in a quantitative determination of pigment weight concentration in the paint; however, the latter two methods lend themselves to chemical analysis of the pigment sample after this determination.

Volatile Concentration

ASTM D 2369 is a standard experimental method to determine the total volatile content of a coating. In contrast, ASTM Practice for Volatile Organic Compound (VOC) Content of Paints and Related Coatings (D 3960), offers a method of calculating the VOC using the nonvolatile content, the water content (if any), and the density of the coating. These latter values are predetermined using referenced ASTM methods, and they are subsequently used in the calculations to determine VOC of the paint. It should be noted that in solvent-borne coatings the VOC is the volatile content; however, water-borne coatings obviously have a nonorganic volatile component which must be taken into account when performing these calculations. The VOC is typically recorded in units of grams of organic volatiles per liter of paint with pounds per gallon used as an alternate.

Chemical Analysis

A variety of methods are used to analyze the chemical composition of aircraft coatings and their components. The specific technique which is selected is determined by the material being analyzed and the level of quantitative or qualitative data required. Some of the more common techniques to analyze polymer and solvent systems are gas chromatography, infrared and ultraviolet spectroscopy, and nuclear magnetic resonance (NMR). Atomic absorption and X-ray spectroscopy are common techniques for determining the chemistry of inorganic pigments. Table 1 provides some of the common ASTM methods used to analyze aircraft coatings.

TABLE 1—Analytical methods for aircraft paint components.

Compound	ASTM Method
Ketones	D 2804: Test Method for Purity of Methyl Ethyl Ketone by Gas Chromatography
Isocyanate	D 3432: Test Method for Unreacted Toluene Diisocyanates in Urethane Prepolymers and Coating Solutions by Gas Chromatography
Water	D 4017: Test Method for Water in Paints and Paint Material by Karl Fischer Method
Lead, Cadmium, and Cobalt	D 3335: Test Method for Low Concentrations of Lead, Cadmium, and Cobalt in Paint by Atomic Absorption Spectroscopy
Chromium	D 3718: Test Method for Low Concentrations of Chromium in Paint by Atomic Absorption Spectroscopy

Because of growing concerns over potentially toxic materials, restrictions are being placed on the lead and chromium content of many aircraft paints. These restrictions are in direct conflict with corrosion control requirements since chromate salts, such as strontium chromate, barium chromate, and zinc chromate, have been shown to be excellent corrosion inhibitors for many metals. Therefore, many specifications require analysis for these pigments to ensure either their presence or their absence. Specific methods to determine lead and chromate content are listed in Table 1.

STORAGE STABILITY

General

The effects of long-term storage on aircraft coating performance are a major concern. Long durations of time and extreme temperatures can have drastic effects on the chemical and physical nature of paints, causing them to have different properties than when they were originally manufactured. Since many aircraft manufacturing, rework, and maintenance activities have paint storage facilities which have only moderate environmental controls, determining the effects of these conditions is necessary. Of primary importance are chemical stability and pigment dispersion. These properties are assessed in the laboratory following long-term and accelerated storage conditions.

Long-Term Evaluation

Methods typically used for determination of stability of aircraft coatings are specified in ASTM Test Method for Package Stability of Paint (D 1849), and Federal Test Method Standard (FTMS) 141 method 3022.1, Storage Stability (Filled Container). In these methods, the packaged coating is allowed to sit undisturbed at ambient conditions for an appropriate period of time. (One year is typical for aircraft coatings.) At that time, the coating is reevaluated to compare its physical and optical properties with those originally found for the as-manufactured material. Other methods may be used to evaluate specific aspects of the material at that time, such as FTMS 141 method 3011.2, Condition in Container, method 3021.1, Skinning, or method 4208, Evaluating Degree of Settling of Paint. In most cases, it is essential that: (1) the paint be free from skinning, (2) the pigment has not reagglomerated or formed a compacted cake at the bottom of the container and it can be easily redispersed to form a consistent mixture, and (3) the applied coating has properties similar to when it was manufactured.

Accelerated Conditions

To speed the evaluation of a coating's behavior under storage conditions, methods have been devised to accelerate this behavior by subjecting the coating to extreme conditions. One common example is specified in FTMS 141 method 3019.1, Storage Stability at Thermal Extremes, which subjects the coating to 49°C (120°F) or −12°C (10°F) for 168 h, depending on the type of storage suspected. Methods involving cyclic exposure to high and low temperatures have also been used. With the development of high-performance waterborne coatings for aerospace applications, one major concern is the freeze-thaw stability of these coatings. ASTM Test Method for Freeze-Thaw Resistance of Water-Borne Paints (D 2243) is used to evaluate coating consistency and performance after 17 h at −18°C (0°F).

Another technique for predicting storage stability of coatings is by evaluating the settling properties of pigments under accelerated conditions. Aircraft coating specifications rarely contain this type of evaluation; however, centrifugation is often used as a research tool to evaluate the tendency of various pigments to settle and compact in specific vehicles. The centrifugal force and the duration are selected on a case by case basis to ascertain differences between systems.

FLASH POINT

General

The flash point of a coating is the minimum fluid temperature at which the solvent vapors are ignited by a spark or flame. It can be predicted roughly as the weighted average of the individual flash points for each of the solvents in a coating formulation. The closed-cup technique is generally preferred since container breakage during shipment and storage often leads to flammable vapors being trapped in a confined space. Naturally, these flash points tend to be lower than the corresponding open-cup values.

Pensky-Martens

The Pensky-Martens test is a closed-cup method that can be conducted on an admixed coating or on one of the separate components in the liquid (uncured) state. The material may be refrigerated to bring it to a temperature below the expected flash point. It is then placed in a closed metal cup, heated slowly while stirring, and periodically exposed to a pilot flame through a shutter mechanism. A thermometer immersed in the fluid measures the coating temperature. The flash point is the minimum temperature at which the solvent vapors ignite,

yielding a large flame that propagates over the surface of the fluid. The procedure is covered in ASTM Test Methods for Flash Point by Pensky-Martens Closed Tester (D 93), Method A for clear coatings and Method B for pigmented coatings.

Setaflash

The Setaflash test uses an enclosed apparatus with automatic controls to determine the flash point. It is easier to operate than the Pensky-Martens tester and utilizes an electric heater for efficient heat transfer and greater accuracy. ASTM Test Methods for Flash Point of Liquids by Setaflash-Closed-Cup Apparatus (D 3278), Method B describes the test procedure.

Tag

The Tag tester is similar to Pensky-Martens, except that the cup is placed in a bath containing a mixture of water and ethylene glycol. Only coatings with no suspended solids (such as, fillers) can be evaluated. ASTM Test Method for Flash Point by Tag Closed Tester (D 56) is the applicable test method.

POT LIFE

Pot life is the length of time in which the flow properties (such as, viscosity) of catalyzed paints will not change within an acceptable range for application. Acceptable coating conditions can vary from no change up to gellation. Pot life requirements in the aerospace industry tend to be controlled by production limitations. Since a normal production work shift is 8 h, many paints have been required to have a pot life spanning this period. More recently, restrictions on the volatile organic content compounds (VOC) of paints have resulted in high solids coatings which tend to inherently possess higher viscosity and shorter pot life (2 to 6 h). Pot life of aircraft coatings is usually determined by measuring viscosity as a function of time after mixing the paint for application. Substantial increases in viscosity are an indication that the pot life is nearly expended.

It should be noted that the issue of pot life can be circumvented via the use of plural-component spray equipment, which is becoming more common in the production painting of aircraft. This equipment stores the various components of a multi-component paint separately and then mixes those components at the desired ratio immediately before or at the spray gun. This equipment not only negates pot life as a factor but also minimizes the amount of catalyzed multi-component paint that is wasted due to unused material. The only drawback is that this equipment is most effectively and efficiently used when large volumes of paint (5 gal or more) are used as opposed to small quantities (1 gal or less), which are typical of touchup maintenance operations.

DRYING TIME

ASTM Test Method for Drying, Curing, or Film Formation of Organic Coatings at Room Temperature (D 1640) defines drying times of paint films. As many as eight stages of the paint drying process are recognized by coatings authorities. Determination of a particular set of drying properties is important for aerospace coatings due to the strict time and processing constraints placed on production and maintenance painting facilities. No particular drying time parameters are universal throughout the aircraft industry. Each paint facility has acceptable limits for these drying properties depending on their function, schedule, and climatic conditions. For example, set-to-touch time may be more important to a small parts shop where components are handled shortly after painting. In contrast, dry-hard times may be paramount at a production facility for painting entire aircraft that must be flown shortly after painting.

Set-to-Touch

A film is set-to-touch when it clings weakly to the finger under gentle pressure but none of the film transfers to the finger. This property indicates that the painted piece can be handled gently, but excessive contact will diminish the quality of the coating. This property may be considered important to shops painting small aircraft components which must be moved from the application area.

Tack-Free

Basically, tack is the tenacity of the film to cling to foreign objects. This component of drying is not considered of major importance in production painting; however, it may be used to ascertain the overall drying characteristics of a coating.

Dry-to-Recoat

This stage of drying is considered to be the most important for painting of aircraft because it is one of the major factors controlling the production rate. Dry-to-recoat is the time at which a second coat, or specified overcoat (such as, topcoat), can be applied without developing irregularities in the coating system, such as lifting, blistering, or loss of adhesion. If overcoated prior to the recoat time, these defects can be caused by a number of factors, one of which is the trapping of solvent in the original coat.

Dry-Hard

The most common technique is to squeeze or pinch the coated surface with the thumb and forefinger with maximum pressure. The dry-hard time is when this procedure can be performed without leaving a permanent mark on the coating surface. This drying stage is also important in production painting of aircraft since painting is usually the last stage of maintenance and the aircraft can be flown after the coating is dry-hard.

FILM THICKNESS

Aircraft coatings are developed and manufactured to be applied within acceptable thickness limits. Coatings which are applied outside of these limits will not exhibit their opti-

mum performance properties. For example, thin coatings may not have the required tensile and shear strength, making them susceptible to cracking and chipping, especially around fastener heads and at panel seams. In contrast, coatings which are too thick may lack flexibility and can exhibit excessive internal stresses. Another important consideration is the excessive weight that coatings add to an aircraft, causing additional fuel consumption. Therefore, coating thickness is diligently controlled and measurements are performed in both the wet and dry states.

Wet coating films are checked for thickness during aircraft application processes using various wet film thickness gages according to ASTM Test Method for Measurement of Wet Film Thickness of Organic Coatings (D 1212). A tooth gage is commonly used in the aerospace industry since it is simple to use, inexpensive, and can be used to obtain good approximations of dry film thickness. These approximations are made by multiplying the wet film thickness by the coating volume percent solids.

The thickness of cured aircraft coatings can be determined either destructively or nondestructively. Destructive methods involve the chipping or cutting of dry films from a substrate and subsequent measurement of the coating thickness with a gage. This approach is typically not taken for aircraft coatings since the coating-substrate bond must be destroyed. Nondestructive techniques include micrometer, eddy current, magnetic induction, and a magneto-resistor/thermistor system. These are the most desirable methods of dry film thickness determination used in the aerospace industry, both in the field and in the laboratory due to their accuracy and ease of use. One problem encountered is that aircraft are constructed of a number of types of materials. Therefore, the method used to determine coating thickness may depend on the substrate material, especially if a nondestructive method is used.

OPTICAL PROPERTIES

General

The appearance of an applied coating is determined by a number of optical properties (color, gloss, opacity, etc.). In the commercial aerospace industry, where public opinion is a consideration, these optical properties can strongly affect the initial impression of the aircraft and are considered to be important with respect to customer recognition. The optical properties of coating systems for military aircraft affect the detectability of these aircraft and thus effect their survivability in potentially threatening scenarios. In both the commercial and military sectors, optical properties are specified with strict tolerances and are closely monitored with instrumentation as well as with the naked eye.

Color

The colors used on commercial aircraft tend to be strong and vibrant for recognition and attraction. The colors of military aircraft coatings are empirically selected in order to achieve either theater-specific (desert, forest, arctic, etc.) or multi-theater (world-wide) camouflage paint scheme requirements. In either case, paint color is considered to be important. In addition, color change is often used to assess the effects of environmental exposure (weathering, immersion in fluids, etc.) on aircraft coatings. Means of characterizing aircraft coating colors range from qualitative visual assessment to quantitative measurements with instruments, the latter providing the obvious advantage of consistent, numerical results. For the latter, ASTM Test Method for Calculation of Color Differences from Instrumentally Measured Color Coordinates (D 2244) is followed, resulting in a color description in either the XYZ or Lab color coordinates. Color differences, as qualified by a delta E value, are determined by using these color coordinates as described elsewhere in this manual to determine delta E.

One additional note must be made with respect to color measurement of aircraft coatings. Colorimeters and spectrophotometers can both be used to quantitatively measure color. Colorimeters use a specified light source with defined radiation wavelengths and intensities, typically resulting in a direct output of XYZ and/or Lab color coordinates. Spectrophotometers measure light reflected from the coating surface over an entire wavelength region. (In the case of color characterization, this is the visible region of the spectrum.) Of the two, colorimeters are less expensive and easier to use. However, colorimeters do not account for metamerism. Metamerism is a phenomenon that occurs when an object appears to be different colors under different light sources. This effect is observed with some coatings for military aircraft, which use unconventional pigments to obtain camouflage properties. In order to confirm that two colors are the same, their total reflectance over the entire visible spectrum must match. These data are obtained using a spectrophotometer. In addition, spectrophotometers are frequently used for military aircraft coatings to determine their reflectance characteristics outside of the visible region, most commonly the infrared and ultraviolet regions.

Opacity (Contrast Ratio)

Opacity or hiding power is the ability of a coating to mask the underlying substrate. Opacity of aircraft coatings is usually quantified by its contrast ratio according to ASTM Test Method for Hiding Power of Paints by Reflectometry (D 2805). In this method, the coating is applied over white and black substrates. (Contrast ratio or Leneta charts are typically used.) A colorimeter is used to measure the coating's luminous reflectance (Y) on the black and white surfaces. Contrast ratio is then determined by:

$$\text{Contrast ratio} = Y(\text{black})/Y(\text{white})$$

Contrast ratio is a function of coating dry film thickness. The method must define the coating thickness at which the contrast ratio is determined; 2.0 mils is common for aircraft topcoats. Applying a coating to a precise thickness is difficult and may require several attempts. An alternative approach is to determine the contrast ratio at several coating thicknesses and subsequently fit the data to a quadratic equation. This equation can then be used to determine the contrast ratio at the desired coating thickness.

Reflectance and Gloss

Incident light which is reflected from a surface has two components, specular and diffuse. Specular reflectance or gloss represents light that has been reflected off a surface when the angle of incidence equals the angle of viewing. Diffuse reflectance is light reflected in all directions other than specular. Specular reflectance data are usually obtained via glossmeters whereas diffuse reflectance data are obtained by the use of goniophotometers.

Gloss of aircraft coatings is measured by instruments that have been standardized to either 60° or 85° incident angles according to ASTM Test Method for Specular Gloss (D 523). Commercial aircraft coatings have high gloss and are usually characterized at 60°. In contrast, many military aircraft are painted with low gloss coatings for camouflage purposes. In addition to gloss analysis at 60°, military coatings are also analyzed at 85° in order to minimize glare at grazing angles.

Directional reflectance represents the optical data that are obtained from analyzing reflected diffuse light. This type of data are normally obtained via goniophotometric equipment. Several methods describe procedures for these measurements, including ASTM Test Method for Directional Reflectance Factor, 45 deg, 0 deg, of Opaque Specimens by Broad-Band Filter Reflectometry (E 1347) and Practice for Goniophotometry of Objects and Materials (E 167). The use of diffuse reflectance of aircraft coatings is typically limited to those for tactical military functions which require camouflage properties.

ADHESION

General

For aircraft coatings to provide maximum protection against degradation, they must firmly adhere to their substrate. Because of the complex nature of adhesion, various techniques have been devised to determine the adhesive characteristics of coatings. Since a coating's adhesion to its substrate can be significantly affected by environmental conditions, these tests are often performed after exposure to accelerated conditions such as immersion in water at elevated temperature. Common adhesion tests used to evaluate aircraft coatings are tape and scrape tests. Other techniques, such as mechanical peel, tensile, and shear tests, are used less frequently.

Tape Tests

Adhesion tape tests are described in ASTM Test Methods for Measuring Adhesion by Tape Test (D 3359). These are the easiest and most versatile of the adhesion tests because they can be conducted in both laboratory and field environments. Tape tests are performed by cutting through the applied coating, into the substrate. A variety of scribe patterns can be used. One common pattern (described in the "A" method of D 3359), which is used to evaluate aircraft coatings, is two scribes forming an "X." An alternative pattern (described in the "B" method of D 3359), is formed by scribing eleven parallel lines through the coating, followed by a second set of eleven lines which are perpendicular to the first set. These scribe lines create a matrix of 100 squares. Adhesive tape is firmly applied over the scribe area and is subsequently removed with a quick upward motion. Coating adhesion is then characterized using standard ratings for the amount of coating removed according to the ASTM method.

As mentioned above, the coated specimens can be subjected to a specific environment prior to testing adhesion characteristics. This practice is most commonly performed with the tape tests. A typical exposure for aerospace coatings is a 24-h immersion in water at 21°C (70°F). More severe exposures are becoming common as coating technology advances. One example is immersion in water at 65°C (150°F) for seven days. Immediately upon removal from the water, the coating is scribed and tested.

Scrape Adhesion Test

The scrape adhesion test is described in ASTM Test Method for Adhesion of Organic Coatings by Scrape Adhesion (D 2197). Scrape adhesion is used to characterize the adhesive and shear strength properties at the primer-substrate interface. The instrument used for this test is the Gardner Labs Scrape Adhesion Test Apparatus (Model SG-1605). The specimen for this test has an area which is uncoated with the substrate exposed. The test is performed by guiding a weighted stylus at a 45° angle to the specimen along the exposed substrate into the coating system. The scrape adhesion value is recorded as the heaviest weight used without shearing the coating from the substrate. Typical scrape adhesion values for aerospace primers fall into the 3 to 5-kg range.

The scrape adhesion test is also used to determine the intercoat adhesion between a topcoat and a primer. When testing this property, a specimen with a section of primer exposed is used and the stylus is guided across the primer into the topcoat. Typical scrape adhesion values for aerospace topcoats also fall into the range of 3 to 5 kg. This test can also be performed after exposure to severe environmental conditions.

Peel and Tensile Tests

Peel test methods are rarely used for aircraft coatings. Instead, a modified version of an adhesive peel test is occasionally used. In this test, two thin metal strips are bonded together using the coating as the adhesive. One end of the specimen is left unbonded, and the metal strips at this end are separated to form a "T." They are subsequently pulled apart in a tensile machine, and the force needed to pull the two strips apart is recorded as the adhesive peel strength of the coating. The type of failure (adhesive or cohesive) is also recorded. An adhesive failure indicates that the coating strength exceeds that of the coating-substrate adhesive strength.

The most common tensile adhesion test used on aerospace coatings is a tensile pull-off test, also referred to as a button test. In this test, a flat head paten is bonded to the surface of the coating with an adhesive. A tensile force is then applied to the paten perpendicular to the coating surface until the paten is removed. The location at which the paten is removed from the surface must be carefully examined. In many cases, the adhesive which bonds the paten to the coating will fail or the coating may fail cohesively. In these cases, it can only be

stated that the adhesive strength of the coating exceeds the tensile strength recorded. Only if the coating fails adhesively is the recorded tensile strength that of the coating-substrate adhesion.

FLEXIBILITY

General

Flexibility is an important property for aerospace coatings, particularly at low temperatures (−51°C), which is common for aircraft cruising at high altitudes. Cracking of coatings at skin joints and around fastener heads can lead to corrosion of exposed areas. Corrosion inhibiting epoxy primers used on aircraft tend to be brittle and exhibit poor flexibility, whereas the urethane topcoats are generally more flexible, especially at low temperatures. Sealant materials and elastomeric primers occasionally are used to improve the overall flexibility of the paint system.

Mandrel Bend

The flexibility of high-performance coatings is commonly characterized by the mandrel bend test method outlined in ASTM Test Methods for Mandrel Bend Test of Attached Organic Coatings (D 522). This test is normally conducted at low temperatures such as −51°C and is performed by bending a painted specimen 180° around mandrels of various diameters with the coating aligned away from the mandrel. After allowing the specimen to return to room temperature, the coating is examined for cracking along the bend. The smallest (most severe) mandrel diameter which the coating can withstand without cracking is recorded. One standard military specification requirement for this test on low gloss coatings is a 2-in. mandrel bend while more flexible coatings can withstand mandrel bends of ⅛ to ¼ in. at low temperatures without cracking.

Impact Tests

The most universal test for measuring impact flexibility of aerospace coatings is Method 6226 (G.E. Impact) of Federal Test Method Standard 141B. The test apparatus consists of a solid steel cylinder weighing 1.69 kg (3.7 lb) which has spherical knobs protruding from the end. These knobs are designed such that the coating system is subjected to elongations of 0.5, 1, 2, 5, 10, 20, 40, and 60%. The impact is accomplished by allowing the steel cylinder to fall freely from a height of 1.05 m (42 in.) through a hollow cylinder guide, striking the reverse uncoated side of the specimen. The imprints formed from the knobs are examined, and the impact elongation is recorded as the highest deformation without cracking of the coating. A standard requirement for this test on aircraft top coats is 20% elongation.

Another commonly used test is the Gardner impact test specified in ASTM Test Method for Resistance of Organic Coatings to the Effects of Rapid Deformation (Impact) (D 2794). This test is performed in a similar fashion to the G.E. impact test described above; however, the weighted cylinder has a rounded end and is dropped from various heights. The weight of the impact cylinder and the highest height that causes no cracking or disbondment of the coating are used to calculate an impact strength, usually in inch-pounds. This test can be performed directly on the coated side of the panel or, like the GE impact test, on the reverse, uncoated side.

Tensile (Elongation) and Fatigue Tests

For aerospace coatings, free films of the coating generally 5 mils thick or greater are prepared and tested for tensile characteristics. Epoxy primers have relatively high tensile strengths (>2500 psi) but very poor elongations (<10%), whereas flexible primers can have elongations exceeding 100%. It should be noted that the rate of deformation has a significant effect on mechanical properties, including tensile, and this must be clearly specified as part of the testing procedure. For this reason, elongations obtained from impact tests cannot usually be directly correlated with those from tension tests.

Fatigue tests are not usually performed to study coating performance. However, fatigue testing of coated specimens with fasteners has been performed to study cracking of aircraft paints around fastener heads. In these studies, increased flexibility of the coating generally leads to less cracking and better overall performance. Isolated studies [*8*] have been reported in which coatings were used as a variable in fatigue testing of metal test fixtures. In these studies, a series of specimens were exposed to a corrosive environment to induce corrosion fatigue. In these cases, flexibility and corrosion inhibition are essential characteristics of the coating.

WEAR RESISTANCE

General

Aircraft coating systems can experience wear due to a number of causes and mechanisms. The most obvious of these is abrasion at leading edges of wings, antennas, and radomes caused by impingement of rain, sleet, dirt, and other debris. Since these leading edges are critical to flight dynamics, special wear-resistant coatings are often applied to these areas to protect the underlying substrate from damage. Another form of wear can be caused from the movement of adjacent parts such as flaps and stabilizers. In addition, internal parts such as bearings may be coated to prevent excessive wear. Since all of these types of wear cause different mechanisms of coating degradation, a number of varying tests are performed to simulate in-service conditions. For example, coatings which protect against rain erosion do not usually protect well against erosion from sand. Specifications for aircraft coatings (other than those for rain erosion) typically do not contain wear tests; however, development and selection of new aerospace coatings often require that characterization of wear properties be performed. Therefore, careful evaluation of wear mechanisms and selection of suitable evaluation methods is essential for these types of coatings.

Rain Erosion

There are a number of facilities throughout the United States which have built equipment to evaluate rain erosion. Some of these facilities are discussed in Refs *9* and *10*. In general, coatings are applied to a small specimen which is subsequently secured to a test fixture arm. The test is performed by spinning this arm in a chamber with falling water droplets that impinge upon the coated surface. Parameters of the test include:

1. Substrate material, thickness, and geometry.
2. Coating type and thickness.
3. Water droplet size and falling rate.
4. Testing arm speed (specimen-water droplet impact).

Although attempts to correlate data from various test rigs have been unsuccessful at obtaining quantitative relationships, trends in coating performance have been observed. These trends generally agree with rain erosion performance on aircraft.

Air Blast

Techniques that are used to evaluate erosion from sand, dirt, and other foreign debris typically involve an air blast to impinge particles on to the coating surface. A common method is ASTM Test Method for Abrasion Resistance of Organic Coatings by Air Blast Abrasive (D 658). This method uses 75-μm silicon carbide particles flowing at a rate of 45 g/min with an air supply pressure of 13 kPa. The method is often modified to evaluate effects of other particles and air pressures. The results can be reported as the weight of debris necessary to abrade a unit film thickness or as the weight loss of coating per weight of abrasive used.

Taber Abraser

ASTM Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser (D 4060) is a frequently used test throughout the coatings industry because it is well defined and relatively easy to perform. As such, it is often used for aircraft coatings to assess their wear characteristics. Care must be taken in interpreting Taber abraser results since reproducibility of data from lab to lab is not consistent.

HARDNESS AND MAR RESISTANCE

Pencil Hardness

The most frequently used test for hardness of aircraft coatings is the pencil hardness test, ASTM Test Method for Film Hardness by Pencil Test (D 3363). Briefly stated, it is performed by guiding pencils of various hardness across a coating surface to determine the hardest pencil that will not scratch or mar the coating. The test is used on aircraft coatings for several reasons, including:

1. To assess coating cure and cure rate.
2. To evaluate the coating's ultimate hardness.
3. To evaluate damage caused by weathering and operational fluids (such as, by comparing coating hardness before and after exposure).

Shore Hardness

The Shore hardness test (ASTM Test Method for Rubber Property-Durometer Hardness (D 2240)) is inappropriate for thin coatings (thickness <6.4 mm or 0.25 in.). However, for thicker coatings such as sealants, ablative, and intumescent materials it can be used to evaluate hardness, cure, and environmental effects.

Arco Microknife

Although the microknife test was originally designed to evaluate adhesive strength of coatings, it has been used to determine hardness. This can be performed by placing a specified weight on the diamond stylus and determining the number of scratch cycles required to cut through the coating. It can also be performed by determining the weight needed to get through the coating with a specified number of cycles.

Mar Resistance

Mar resistance is not usually considered a critical property for aircraft coatings. One method is the balance beam test that uses the scrape adhesion apparatus described in ASTM Test Methods for Adhesion of Organic Coatings by Scrape Adhesion (D 2197). The method determines the weight required to mar a coating surface with a stylus.

CORROSION INHIBITION

Salt Spray

Corrosion resistance is an important property for aerospace coatings, and numerous tests have been developed to evaluate the corrosion preventive properties of coatings, ranging from simple exposure studies to sophisticated electrochemical analysis.

Salt spray tests are commonly used as accelerated corrosion resistance tests for coatings. The two primary methods used for aircraft coating systems are the 5% NaCl neutral salt spray test covered by ASTM Test Method of Salt Spray (Fog) Testing (B 117) and the acidified SO_2/salt spray test covered by ASTM Practice for Modified Salt Spray (Fog) Testing (G 85). Specimens coated with an aircraft finishing system are usually scribed with an "X" through the coating into the substrate and then exposed for various times (usually 1000 to 3000 h for ASTM B 117 and 48 to 1000 h for ASTM G 85). Exposure periods for coatings vary for different substrate materials and can be selected either as a specified duration or as the point where significant differences in finishing system performance are observed. After exposure, the panels are inspected for corrosion in the scribe area and blistering or uplifting of the coating across the specimen. Subsequently, the coatings can be carefully removed from the surface without disturbing the underlying substrate by using a chemical stripper, and the specimen surface can be examined for evidence of corrosion.

Standard aircraft epoxy primer/polyurethane topcoat systems perform well on aluminum substrates in the neutral test, normally exhibiting no significant corrosion products in the scribe or any blistering of the coating after 1000 h. These

materials may last up to 3000 h without any evidence of corrosion. The SO_2/salt spray environment simulates stack gases such as those found in industrial areas and on diesel-powered aircraft carriers. It is an extremely aggressive environment, and aircraft systems exposed to this environment tend to fail at much shorter times than in the neutral test. A system exhibiting no significant corrosion products or blistering after 500 h is normally considered acceptable in this acidified environment.

Because numerous materials are used in the construction of aircraft, the contact of dissimilar materials is common. When this occurs, the potential for galvanic corrosion is high if the two dissimilar materials are not insulated from each other. In many cases, organic coatings are applied to provide this insulation. Therefore, it is becoming common to assess the ability of aircraft coatings to inhibit galvanic corrosion by painting and exposing specimens containing dissimilar materials. One example is a graphite-epoxy composite coupled to aluminum.

Immersion Studies

Total immersion corrosion tests can be severe depending on the immersion solution, duration, and exposure temperature. Again, blistering or uplifting of the coating or corrosion of the underlying substrate constitutes failure in this test. Although this type of evaluation is not typically performed on aircraft paints, coatings requiring a high degree of impermeability, like those used in or around aircraft bilge areas, galley, lavatories, and other areas where water can be entrapped, would be evaluated with this type of test.

Filiform Corrosion

Filiform corrosion occurs on painted aluminum, steel, and magnesium in a high-humidity and elevated temperature environment containing oxygen and chloride ions. Filiform initiates at points where the coating ruptures (commonly around fastener patterns or panel seams) and propagates as filaments under the coating. If unchecked, damage of the coating system can allow other corrosion mechanisms such as stress corrosion cracking, exfoliation, and crevice corrosion to ensue. Typical filiform corrosion tests involve exposing coated specimens to hydrogen chloride vapors and then placing them into a high-humidity (85 to 95% RH) and elevated temperature (85 to 140°F) environment for a specified duration such as 1000 h. It should be noted that this type of corrosion is prominent on pure aluminum. For this reason, the test is performed on aluminum clad specimens in lieu of aluminum alloy.

Electrochemical Analysis

Reference *11* provides a thorough review of electrochemical methods used to evaluate the performance of corrosion protective coatings. Of these methods, electrochemical impedance spectroscopy (EIS) is one of the most promising techniques because it provides both qualitative and quantitative information about the corrosion resistance properties of the coatings and the substrates to which they are applied. In addition, EIS can give insight on the nature of their interfacial adhesion. References *12* and *13* provide detailed descriptions of EIS and its application for analyzing organic coating/metal substrate systems. EIS measurements can be made using equipment like EG&G Princeton Applied Research Corp. (PARC) Model M388 Impedance System. Test cells consist of a glass o-ring joint clamped onto a coated metal specimen [*12*]. Electrolytes used for specimen exposure can range from distilled water to neutral or low pH salt solutions.

For an EIS experiment, the test cell described above is filled with the selected electrolyte solution. A reference electrode (such as, Calomel) and a counter electrode (such as, platinum or graphite) are immersed in the cell with the metal substrate serving as the working electrode. The EIS cell is allowed to reach equilibrium as indicated by its open circuit potential or steady-state rest potential. Small excitation amplitudes, usually in the 5 to 10-mV range, are introduced to the system, and the response signal is measured. These data can be correlated to an electrical circuit consisting of resistors and capacitors. The information from this electrical circuit is a model depicting the electrochemical reactions occurring in the coating-substrate system. Because of the detailed quantitative information that is obtained from EIS analysis, it's use as a tool to research high-performance aircraft coatings is growing. In many cases, attempts are made to correlate EIS data with results from other corrosion studies such as salt spray. This approach provides a detailed assessment of coating integrity, durability, and corrosion inhibition.

WEATHERING AND ENVIRONMENTAL EXPOSURE

Outdoor Exposure

Outdoor exposure tests are normally conducted over periods of one year or more. In an effort to produce timely results, these tests are not frequently performed on aircraft coatings. However, one common specification for an aerospace topcoat, MIL-C-83286, does require a one year exposure of coated panels on an outdoor test rack in Florida. It is specified that the panels must be at a 45° angle and facing south. After this exposure period, the coating is evaluated for changes in color, gloss, and flexibility.

The U.S. Navy has instituted a program to evaluate the exterior durability of coatings in its operational environment by placing exposure racks on aircraft carriers and other ships. Results of these exposures have resulted in identification of successful aircraft coatings. Details of this effort are provided in Ref *14*.

Accelerated Weathering

The components of outdoor natural weathering which have the most significant effects on coatings and other materials are ultraviolet radiation and water (humidity, condensation, rain, etc.). It has been proposed that these conditions can be simulated and that the resulting effects can be accelerated by subjecting coatings and other materials to high-intensity light (including ultraviolet wavelengths) and water.

The most common accelerated weathering methods used for aircraft coatings are the xenon-arc Weatherometer and

the QUV accelerated weathering tester. The former method is described in ASTM Practice for Operating Light-Exposure Apparatus (Xenon-Arc Type) with and Without Water for Exposure of Nonmetallic Materials (G 26). Again, there are a number of test variables which have significant effects on coating performance, and various laboratories have adopted slightly different procedures and parameters. Since there are no precise correlations between natural weathering and any of the accelerated methods for aircraft coatings, it is especially important that the test variables are well defined. One common approach that is used in military and federal specifications (MIL-C-85285, Coating, Polyurethane, High Solids and TT-P-2756, Polyurethane Coating: Self-Priming Topcoat, Low VOC) follows ASTM G 26, Type BF as a guideline. The exposure is performed in a 6000-W, xenon arc weatherometer with a continuous cycle consisting of 102 min of high-intensity light only and 18 min of light and water spray. The conditions in the chamber are as follows:

1. Black body temperature	60°C (140°F)
2. Relative humidity	50%
3. Intensity of the arc wavelength	0.55 W per m^2 at 340 nm

The exposure period is 500 h, and the coating is subsequently evaluated for changes in gloss, color, and flexibility.

The second common method for accelerated weathering is described in ASTM Practice for Operating Light- and Water-Exposure Apparatus (Fluorescent UV-Condensation Type) for Exposure of Nonmetallic Materials (G 53). In this case, specimens are subjected to periods of ultraviolet light and condensation, respectively. During the condensation period, the coating surface is exposed to 100% relative humidity at elevated temperature, while the back side of the specimen is exposed to cooler air, thus producing water condensate on the coating. Exposure parameters include UV intensity, duration of exposure to each condition, and temperature of the chamber and condensate.

Humidity

Since high temperature and humidity can cause coating disbondment and substrate corrosion, extreme humidity exposure is often performed on aircraft coatings to evaluate their resistance to such environments. Again, exposure parameters vary and must be clearly specified for reproducibility and interpretation of results. ASTM Practice for Testing Water Resistance of Coatings in 100% Relative Humidity (D 2247) is usually followed. The chamber conditions are 49°C (120°F) and 100% relative humidity with constant condensation on the coated panels. A typical exposure period can range from 30 to 90 days.

FLUID RESISTANCE

Aircraft coatings are frequently subjected to aggressive operational and environmental fluids. Several examples are hydraulic fluids, engine oils, fuel, deicing solutions, and cleaners. In order to assess the resistance of aircraft coatings to these fluids, a number of exposure tests are performed. The exposure can range from a simple wiping action to long-term immersion. The temperature of the exposure is also a critical variable. Following exposure, the specimen is usually evaluated for degradation of the coating (discoloration, softening, blistering, etc.) and substrate (corrosion).

Water Resistance

Resistance to water is usually performed by total immersion. The severity of the exposure can range from 24 h at ambient temperatures to seven days at 65°C (150°F). Since water can play a significant role in coating disbondment [*15*], adhesion tests are frequently performed immediately upon removal of the coated specimen from water immersion.

Another technique is to measure the water absorption (uptake) of a coating as a function of immersion time. This is performed by simply weighing the coated panel (or free film) as a function of immersion time. Water up-take values for high-performance aircraft coatings can range up to 20%.

A third technique to characterize the effects of water on a coating is to determine its water vapor transmission rate (WVTR). WVTR is a measure of the rate at which water will permeate through a coating. ASTM Test Method for Water Vapor Transmission of Organic Coating Films (D 1653) describes two methods to determine WVTR. In Method "A," a free film of the coating is sealed to the open mouth of a cup containing distilled water. In Method "B," the free film is sealed to a cup containing desiccant. These fixtures are exposed to controlled environments (temperature and humidity), and they are weighed periodically to determine the rate of water vapor diffusion through the coating. Aircraft coatings must exhibit low WVTRs to maintain their adhesion and corrosion inhibition.

Organic Solvent Resistance

Resistance to organic solvents is usually performed by rubbing a coated panel with a cloth dampened with a specified solvent. Since toluene and methyl ethyl ketone (MEK) are both harsh and have been frequently used in the aerospace industry, they are common solvents. After rubbing the surface, the coating is inspected for color change, dissolution, or any abnormality which may have been caused by the solvent. The cloth can also be inspected for residue which may be apparent by a color change.

Hydraulic Fluids and Engine Oils

Hydraulic fluids and engine oils are frequently used at elevated temperatures, and therefore their attack on aircraft coatings can be accelerated and more severe. Table 2 describes typical immersion tests using these fluids.

HEAT RESISTANCE

Aerodynamic heating can produce skin temperatures of 121°C (250°F) in level flight and 176°C (350°F) during high-speed maneuvers. Painted components adjacent to engines and exhaust tracks may experience unusually high temperatures. This heat may exceed the maximum service temperature of some organic coatings, which may cause darkening, embrittlement, and/or premature aging. The heat resistance

TABLE 2—Aircraft operational fluid immersion tests.

Material Duration	Temperature
Lubricating oil (MIL-L-23699) Hours: 24	121°C (250°F)
Hydraulic fluid (MIL-H-83282) Hours: 24	66°C (150°F)
Fire-resistant hydraulic fluid Days: 7	21°C (70°F)
Jet fuel (JP-4, JP-5) Days: 7	21°C (70°F)

of a coating is determined by subjecting a coated panel to a constant temperature for a specific period of time. For example, specification MIL-C-85285B requires that a polyurethane topcoat withstand exposure to a 121°C (250°F) oven for 1 h without a significant color change (maximum delta E value of 1.0).

Thermal Fatigue

Thermal fatigue refers to the resistance of a coating to stresses induced by rapid temperature changes. Often called thermal shock, this simulates the effect of take-off from hot (and sometimes humid) ground temperatures to the cold atmosphere at high altitudes and then back again. The MIL-C-81945B intumescent coating used on weapons must withstand 60°C (140°F), 95% relative humidity for 24 h followed by −40°C (−40°F) for 24 h. The coating is then cycled between the two chambers for 28 days. Cracks extending deep into the coating indicate failure in this test. Method 503.1 of MIL-STD-810 provides further guidance.

Thermal Conductivity

Stored weapons (bombs, missiles, etc.), including those used on military aircraft, must be protected from accidental fuel fires. This is accomplished with exterior, insulating coatings on those weapons that delay ordnance reactions and provide fire fighters sufficient time to extinguish the fire. The efficiency of these coatings is measured by a unique test, originally developed by NASA [*16*]. It uses a small furnace burning JP-4 or JP-5 aviation fuel to produce a constant heat-flux of 10 btu/ft^2-s at a flame temperature of approximately 1800°F (982°C). A coated panel is mounted to an open port above the furnace, and the temperature of the uncoated backside is recorded as a function of time. The thermal efficiency is calculated from these data. It is expressed as the number of seconds/mil of coating thickness for the backside temperature to reach either 500°F (260°C) or 1000°F (537°C). (Most explosives and propellants react between these two temperatures.) Specification MIL-C-81945B requires that intumescent coatings have a minimum thermal efficiency of 2 s/mil to 500°F (260°C).

STRIPPABILITY

Aircraft are periodically returned to depot maintenance facilities for inspection and overhaul. At this time, the aircraft's exterior coating system is removed by chemical and/or mechanical means. In order to insure that this procedure can be adequately performed, strippability tests are conducted in the laboratory as part of the coating evaluation procedure. One common testing procedure is accomplished by applying a chemical paint stripper, such as MIL-R-81294, onto the surface of a coated specimen. After a specified period of time (usually 1 h), the panel is abraded with a stiff bristle brush and rinsed with water to remove loosened paint. Usually, 90% removal of the coating from the substrate is considered acceptable.

CLEANABILITY

Low-gloss aircraft coatings, such as those used in camouflage schemes on military aircraft, become dirtier and are more difficult to clean and restore than high-gloss coatings. This is primarily due to the increased surface roughness of low-gloss coatings, which entraps carbonaceous and oily soils as discussed in References *17* and *18*.

The cleanability or the ease at which dirt and soil can be removed from a coating surface can be quantified by consistently soiling a coating and using a standard cleaner and cleaning motion in attempts to remove this soil. Measuring the color difference of the coating prior to soiling and subsequent to cleaning provides an indication of the coatings cleanability. The following is a detailed procedure for the evaluation of the cleanability of aircraft coatings. The soil in this procedure was generated using a hydraulic fluid. This soil is representative of that found on operational aircraft. Other soils can be derived from greases and lubricating oils.

APPARATUS REQUIRED

1. Test panels 7.62 by 15.24 by 0.05 cm (3 by 6 by 0.02 in.) of 2024 T3 aluminum alloy chromate conversion coated with materials conforming to military specification MIL-C-81706 to produce a coating meeting MIL-C-5541.
2. One-liter, wide-mouth, glass jars.
3. Balance, accurate to 0.1 g.
4. High shear mixer.
5. Hog bristle brush (Gardner WG-2000-B).
6. Acid brushes.
7. Rubber roller, 2270 g (5 lb).
8. Forced draft oven capable of 105°C (221°F).
9. Wear tester (Gardner Heavy Duty Wear Tester).
10. Template for positioning and holding test panels on the wear tester.
11. Cellulose sponge backed with nylon web (Scotch Brite 63).

PREPARATION OF SOIL

1. Place 50 g of carbon black (such as Raven 1040 manufactured by Columbian Chemical Company) in 500 g of hydraulic fluid meeting military specification MIL-C-83282.
2. Homogenize the carbon black and hydraulic fluid mixture using a high shear mixer for 15 min. Prior to application of the soil to the specimen, thoroughly stir or shake the mixture to obtain a thorough dispersion.

PREPARATION OF THE CONTROL FORMULA CLEANER

1. Any desired aircraft cleaned can be used. However, the following is a control formulation meeting a common aircraft cleaner (MIL-C-85570, Type II) as listed in Paragraph 4.6.13.1 of the specification.
2. Mix the first five ingredients listed below, then neutralize the mixture to a pH of 8.0 with acetic acid. Mix the last two ingredients together and then add that to the initial mixture.

Igepal CO-630 (1)	10.0 parts by weight
Monamid 150 CW (2)	5.0
Dipropylene glycol methyl ether	10.0
Deionized water	71.5
Benzotriazole	0.5
Hostacor 2098 (3)	2.0
Morphaline	1.0

(1) GAF Corporation, or equivalent.
(2) Mona Industries Inc., or equivalent.
(3) American Hoechst Corp., or equivalent.

PREPARATION OF TEST PANELS

1. To the chromate conversion coated aluminum specimens described, apply a suitable primer for the desired topcoat. One such material is epoxy primer conforming to MIL-P-23377 Type I or II to a thickness of 15.2 to 22.9 μm (0.6 to 0.9 mil). Allow to dry for 1 h at ambient conditions. Apply the desired topcoat to the intended thickness. Allow the coating to cure under the appropriate conditions.
2. After allowing the desired cure time and conditions, use a bristle acid brush to coat the painted surface of a test panel with the soil described in the "Preparation of Soil" section. Remove excess soil by covering the test panel surface with tissue and exerting pressure by rolling the tissue with the roller. Repeat this blotting three times using fresh tissue each time. Brush the soiled surface ten times in one direction only, parallel to the long dimension of the test panel, using the hog bristle brush. Bake the test panel at 105°C (221°F) for 60 min.
3. Measure the L, a, and b tristimulus values on a suitable colorimeter and record the values as L_i, a_i, and b_i, respectively.

CLEANING PROCEDURE

1. Dilute the control cleaner by one part cleaner with nine parts distilled water (by volume).
2. Clean the test panel within 4 h using the wear tester as follows. Cut the sponge with any texture "ribs" running perpendicular to the cleaning stroke. When the dry sponge is attached to the cleaning head on the wear tester, the combined weight shall be between 1350 and 1400 g. Place the soiled test panel in the template at an angle 45° to the cleaning stroke. Saturate the sponge and cover the test panel with the diluted cleaner. After 55 to 65 s, clean the test panel using 5 cycles (10 strokes) of the wear tester, then immediately turn the test panel 90° in the template and clean for an additional 5 cycles. Rinse the test panel under a flowing stream of tap water at room temperature for 2 min and allow to fully dry.
3. Measure the L, a, and b values on the sam colorimeter used prior to the cleaning procedure and record them as L_f, a_f, and b_f, respectively.
4. Calculate the change in color due to soiling and cleaning according to the following equation

$$\text{DELTA E} = [(L_f - L_i)^2 + (a_f - a_i)^2 + (b_f - b_i)^2]^{0.5}$$

5. A minimum of three replicates should be tested for each coating at each condition.

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Architectural Coatings

by Harry E. Ashton[1]

INTRODUCTION

Definition and Scope

THIS CHAPTER IS CONCERNED with the selection and use of procedures for testing organic finishes intended for use on interior surfaces, exterior surfaces, or both interior and exterior surfaces. Coatings comprise more than "paints" since the latter are only one kind of coating as defined in ASTM Terminology Relating to Paint, Varnish, Lacquer, and Related Products (D 16):

> "*coating*—a liquid, liquefiable or mastic composition that is converted to a solid protective, decorative, or functional adherent film after application as a thin layer."
>
> "*paint*, n, specific—a classification sometimes employed to distinguish pigmented drying oil coatings ("paints") from synthetic enamels and lacquers."

Definitions used by the Federation of Societies for Coating Technology (FSCT) [*1*] for these terms are:

> "*Coating* (1) Generic term for paints, lacquers, enamels, printing inks, etc. (2) A liquid, liquefiable or mastic composition which is converted to a solid protective, decorative, or functional adherent film after application as a thin layer."
>
> "*Paint* (2) Noun. Any pigmented liquid, liquefiable, or mastic composition designed for application to a substrate in a thin layer which is converted to an opaque solid film after application. Used for protection, decoration or identification, or to serve some functional purpose such as the filling or concealing of surface irregularities, the modification of light and heat radiation characteristics, etc."

Hence, clear varnishes and lacquers are familiar types of coatings that are not, strictly speaking, paints. As one company has proudly, if not grammatically, referred to their products, "Plain Paint It Ain't."

Since there are many different types of coatings, it is useful to classify them into groups. This can be done in several ways as for example according to:

1. *Appearance*—clear, high gloss, metallic, pigmented, red, stain, textured, etc.
2. *Composition*—alkyd, latex, oil, solvent-borne, zinc-rich, etc.
3. *End use*—service location (interior, exterior), end user (industrial, painter, home), specific substrate (wood, metal, masonry), type of object (transportation, bridge, house), particular exposure (marine, below-grade), etc.
4. *Method of cure*—air-dry, bake, cold-cure, radiation-cure, etc.

At times the terminology used in the coating industry can seem confusing to a tyro in the field. For example, an aluminum finish may be used for application to aluminum objects or it may contain aluminum pigment and be used on various objects. Although an automotive coating is intended for application to automobiles, an architectural coating is not similarly intended for architects. Rather, an architectural coating is for the type of structure customarily designed by architects in contrast to those designed by civil engineers. Another designation intended to reduce this potential confusion is "trade sales coatings" that are coatings marketed through retail-trade stores, in contrast to "industrial sales coatings" that are usually marketed directly to the end user.

The definition for *architectural coating* given in the two ASTM standards, D 5146 and D 5324, referred to below, combines the definition from ASTM D 16 with that in the FSCT's Paint/Coatings Dictionary [*1*] as follows:

> "Organic coatings intended for on-site application to interior or exterior surfaces of residential, commercial, institutional, or industrial buildings, in contrast to industrial coatings. They are protective and decorative finishes applied at ambient temperatures. Often called Trade Sales Coatings."

As with many types of coatings, the titles of the two ASTM guides reflect the two main composition categories—waterborne and solvent-borne. These categories indicate the type of volatile material used, both in manufacturing and in application, to reduce the film-forming ingredients to a suitable application viscosity.

Scope

The intended uses and generic gloss range for conventional types of architectural coatings are as follows:

1. Interior finishes, low-gloss.
2. Interior finishes, semigloss and full-gloss.
3. Exterior house and trim coatings, low semigloss to moderate gloss.
4. Exterior and/or interior floor finishes, gloss varies with the particular type of finish.

[1]Senior research officer (retired), Building Materials Section, Institute for Research in Construction, National Research Council, Ottawa, Ontario, K1A 0R6 Canada.

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Each of these finishes is intended for application by brushing, rolling, spraying, or other means to the substrates appropriate to its end use, which may include wood, plaster, masonry, wallboard, steel, previously painted surfaces, and other architectural substrates.

One type of architectural interior coating differing from the generally accepted commercial types is called "high performance architectural coating (HIPAC)." Such coatings are extra-durable systems applied as continuous films that cure to hard, tough finishes that are resistant to abrasion, staining, chemicals, detergents, and mildew growth. Coatings of this type usually are two-component epoxides or urethanes, or are moisture-cure urethanes. Other polymer types are not excluded from this high-performance area if they can be formulated into coatings that meet purchaser performance requirements. As with many conventional coatings, these high-performance coatings are formulated at gloss levels that range from very high to satin (low semigloss).

ASTM GUIDES TO TESTING ARCHITECTURAL COATINGS

The ASTM guides listed below provide systematic compilations of relevant properties, the related test methods, and, where possible, typical values, for the guidance of users.

ASTM D 3730: Guide for Testing High-Performance Interior Architectural Wall Coatings

ASTM D 5146: Guide for Testing Solvent-Borne Architectural Coatings

ASTM D 5324: Guide for Testing Water-Borne Architectural Coatings

CONDITIONS AFFECTING THE USE OF ORGANIC COATINGS

Substrate Types

Substrates may be wood products, masonry, bare plaster, metal, wallboard, and even plastic. The nature of the substrate can affect the application and appearance properties of a coating, such as uniformity and gloss, and is an important factor in determining the type of coating to use. Specific examples of this are:

1. A primer-sealer may be required for porous substrates, such as unpainted drywall, new wood, plaster, or porous masonry.
2. Finishes intended only for interior service do not require resistance to weather factors.
3. Low-gloss wall finishes do not need the abrasion resistance required of floor coatings.

Other factors of importance are the quality of the substrate, which with wood products relates to grain, knots, and compositional structure, and with masonry and plaster products relates to the degree of porosity and alkalinity.

Substrate Conditions

The condition of the surface is important in determining the type of coating and surface preparation that might be required. These conditions include porosity, presence of grease, dirt, mold, water-soluble or oily contaminants, and chalking or flaking of previous coatings. The smoothness of the substrate affects the spreading rate, texture, and final appearance of the coating. Building defects arising from poor construction or deterioration in service or direct contact of the substrate with the ground can result in persistent exposure of the coating to interior or exterior moisture with resultant failure by blistering, flaking, or peeling. Similar failures can occur where painted lumber is adjacent to damp masonry surfaces. Weathering of wood before painting probably will adversely affect the performance of exterior coatings. However, some degree of weathering of masonry surfaces may have a beneficial effect on performance by passivating the surface and changing the alkalinity.

Exterior Coatings

The durability and appearance of these coatings can be affected by short- and long-term environmental conditions. Surface dampness during application and drying can adversely affect the adhesion of solvent-borne coatings but not of water-borne coatings. However, low temperatures during the drying stage can prevent water-dispersed (latex) coatings from forming cohesive films. Of course, no water-borne coating can be applied at temperatures below the freezing point of water. A sunny service environment can be expected to encourage chalking and other forms of film deterioration. In contrast, a shady location, such as on the north side of a structure or nearby trees and shrubs, can protect the film from sunlight but it can promote mildew growth. Orientation of the coating toward sun or shade varies on different parts of a building, e.g., fascia boards and porches.

Interior Coatings

The porosity, smoothness, and color of the surfaces are important factors for both new and repaint jobs. On new construction, low temperatures must be avoided when applying water-borne finishes, and painting is preferably done at normal room temperature. If drying temperatures are too low, long drying times are needed and this can result in significant dust and dirt accumulation on the film. If drying temperatures are too high, the film will dry too rapidly and side-by-side application areas may appear different because they did not flow into each other. High relative humidity is also to be avoided when applying both solvent- and water-borne coatings. Primer coats should be allowed adequate time to dry before applying the next coat.

General

It should be recognized that proper surface preparation and correct application techniques are as important as the inherent properties of a coating in contributing to adequate performance. This is especially true for high-performance coatings. After selecting the best material for a given service, it is essential that the manufacturer's instructions be followed.

SELECTION OF TESTS

Service Location

Because coatings on different surfaces, e.g., ceiling, floor, wall, and in different service environments, e.g., exterior or interior, are subjected to a variety of conditions, specialized coatings have been developed. The test methods discussed in this chapter cover practically all of the properties of architectural coatings. Not all of the tests are needed with any one coating type or location. Coatings intended for exterior use only or for both exterior and interior uses require certain properties not relevant to those intended for interior use only. Property selection and methods of testing for these properties must be governed by experience and the requirements in each individual case and, preferably, by agreement between purchaser and seller.

Value Judgments

The purchaser should first determine the properties required of a coating and then select only the test methods appropriate for those properties. After test selection the purchaser should decide which properties are most important and establish specification requirements accordingly. Since coating properties frequently tend to oppose each other, such as low sheen versus good cleansability or good sag resistance versus good leveling, some properties may need to be less emphasized if others are to be accentuated. This balance of properties must be considered when selecting the tests and establishing the requirements. No attempt is made herein or in the ASTM standard guides listed above to indicate relative importance of the various tests. Also, the referenced standards do not recommend specific test values because properties considered very important by one purchaser may be less so to another.

PROPERTIES OF LIQUID COATINGS

Density

While density, measured in pounds per gallon or kilograms per liter (≡g/mL), has no relation to the quality of a coating, it can be used by the purchaser to ensure product uniformity from batch to batch. In production control, density provides a simple check against the formula weight since any significant deviation indicates an incorrectly made or mixed coating, including the presence of entrapped air. Density is generally measured with a pycnometer, a container of precisely known or measurable volume with a capillary cover through which surplus liquid is expelled as the test temperature, normally 77°F (25°C), is approached. Laboratory pycnometers are typically made of glass and have a narrow neck to reduce evaporation of volatile fluids.

The coating industry uses a special type of pycnometer called a "weight-per-gallon" (mass per unit volume) cup. It is a plastic or metal wide-mouth cylinder, a shape convenient for handling viscous coatings and polymers. Weight-per-gallon cups are usually made to hold 83.454 mL so that the weight in grams required to fill the cup divided by 10 is the density in lb/U.S. gallon, or to hold 100 mL so that dividing the weight by 100 results in g/mL or by 10 yields lb/Imperial gallon. The density of water at the test temperature is used for precise work or to establish a correction factor if the device is worn, damaged, or dirty from poor cleaning in a way that effectively changes the internal volume of the cup. Typical coating densities are in the range of 10 to 12.5 lb/U.S. gallon (1.2 to 1.5 kg/L) for water-borne paints. Solvent-borne coatings are in the 8 to 10 lb/U.S. gallon (0.9 to 1.2 kg/L) range due to the lower density of the solvents used instead of water. Instructions for carrying out the test are given in ASTM Test Method for Density of Paint, Varnish, Lacquer, and Related Products (D 1475). Other devices and methods for measuring density are presented elsewhere in the manual.

Coarse Particles

To form uniform films with good appearance, liquid coatings must be free of coarse particles and foreign matter. In general the glossier the film, the more detrimental such particles are to appearance. These particles are far larger than those determined in the fineness of dispersion method described below. They normally occur as a defect in the production process that permits introduction of clumps of dry pigment or foreign matter such as pieces of shipping bags and the like. The content of objectionable material is determined with ASTM Test Methods for Coarse Particles in Pigments, Pastes, and Paints (D 185) by straining the diluted coating through a 325-mesh (45-μm) screen and weighing the amount retained. A typical maximum requirement is 0.5% by weight. Objects such as pigment lumps, polymer seeds, etc. with a generally spherical shape are retained on such a screen. Linear objects like fiber strings can flow through this screen and may require other removal methods, such as centrifuging. Screens are inexpensive and readily available, and results obtained with them are easy to comprehend. Devices such as centrifuges are more expensive and more time consuming than screens, but they often yield more accurate results than the latter.

Fineness of Dispersion

Generally, the more finely a pigment is dispersed, the more efficiently it is being utilized. Also, if pigment agglomerates exceed the thickness of the dry film, it will be impossible to obtain a coating of the desired degree of smoothness. One method for measuring the degree of dispersion, commonly referred to as "fineness of grind," is to draw the liquid coating down a calibrated tapered groove varying in depth from 4 to zero mils (100 to zero μm), which is equivalent to zero to 8 Hegman units. The depth at which continuous groupings of particles or agglomerates protrude through the surface of the wet film is taken as the fineness of dispersion value. Good dispersion is indicated by high readings in Hegman units or low readings in mils or micrometres. Lower gloss finishes do not generally require a fine dispersion, so they might have a dispersion value of 2.5 mils (65 μm or 3 Hegman units). Some interior flat latex paints have finenesses as low as 3.5 mils (90 μm or 1 Hegman unit). Most interior semigloss and gloss enamels have a fineness value of about 1.5 to 0.3 mils (40 to 7 μm or 5 to 7.5 Hegman units), although some full gloss coatings might be near zero in depth, equivalent to 8

Hegman units or as fine as can be measured by this method. Information about conducting the test appears in ASTM Test Method for Fineness of Dispersion of Pigment-Vehicle Systems (D 1210).

Flash Point

This is almost exclusively a concern with solvent-borne coatings. The organic solvents used in these coatings have characteristic temperatures at which their vapors support combustion. This temperature is known as the flash point and is often used for hazard classification in shipping by common carrier. It is also used to determine conditions of storage to meet fire regulations and the U.S. Occupational Safety and Health Act (OSHA). There are several accepted ways for measuring flash point that give somewhat different results. For pigmented and/or viscous materials that require stirring to obtain consistent results, ASTM Test Methods for Flash Point by Pensky-Martens Closed Tester (D 93, Method B) is specified. The small specimen size used with ASTM Test Methods for Flash Point of Liquids by Setaflash-Closed Cup Apparatus (D 3278) eliminates the need for stirring. Since solvents do not require stirring, they are generally tested with ASTM Test Method for Flash Point by Tag Closed Tester (D 56).

Manufacturers of coatings do not always determine the flash points of their products, but classify them on the basis of the solvents they contain. Since this routine does not detect inadvertent contamination, large-volume purchases are sometimes tested for flash point, in some cases after thinning at the job site. Further details about this technique can be found elsewhere in this manual.

Odor

Some solvent combinations produce undesirable odors, particularly when painting indoors with inadequate ventilation and at elevated temperatures. Although interior solvent-borne coatings usually contain low-odor or odorless mineral spirits, they should nevertheless be evaluated for odor. Latex or other water-borne coatings, which contain relatively little if any organic solvent, may contain other ingredients such as ammonia, residual monomer, etc., that might also be objectionable in a confined space. Hence both solvent- and water-borne coatings should be tested to establish whether the odor is irritating or merely unpleasant.

Although not specifically designed for liquid coatings, ASTM Test Method for Odor of Volatile Solvents and Diluents (D 1296) could be a suitable basis for the evaluation. This method is a comparative procedure for observing characteristic and residual odors of volatile organic solvents and is not designed to determine subtle odor differences or odor intensity. There are hazards associated with the test, and the Hazards section of the method should be read and heeded when the test is used. ASTM D 1296 has been approved as a replacement for Method 4401 of U.S. Federal Test Methods Standard (FTMS) No. 141 by the U.S. Department of Defense.

Volatile Organic Compound (VOC)

Volatile organic compounds evaporate into the atmosphere when coatings dry and/or cure, and they are believed to contribute significantly to air pollution. The chief offenders in this regard are solvent-borne coatings, although water-borne coatings certainly contain some amounts of VOC. In addition, many types of coatings that cure by chemical reaction, in contrast to those that dry solely by evaporation of organic solvent or water, generate volatile molecules such as formaldehyde and related compounds. Both types of materials react with each other and atmospheric oxygen in the presence of sunlight (i.e., photochemical reaction) to produce in the lower atmosphere the actual pollutants, one of which is ozone. Some of the VOCs have also been related to the destruction of ozone in the upper atmosphere. Organic volatiles that are considered to have negligible photochemical activity have, at least to the time of writing, not been included in the calculation of the VOC of a coating for regulatory purposes. Such exempt solvents are very few and within a relatively short time there may be none at all. California and its local agencies have been particularly active in specifying and enforcing limits on the amount of VOC in coatings. Examples of such restrictions are maxima of 350 g/L for "clear wood finishes" and 400 g/L for quick-drying enamels. Since other states have established their own limits, a national rule on VOC in architectural and industrial coatings is at present being developed between representatives of the paint industry and the U.S. Environmental Protection Agency (EPA). ASTM Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings (D 3960), U.S.A. EPA approved, and the recent manual by Brezinski [*2*] discuss applicable ASTM test methods, provide equations for calculating the VOC content in different ways, and provide other information valuable in this area.

Dilution Stability

This property is of concern primarily with solvent-borne coatings because of the wide differences in solubility characteristics of the binders and the solvent power of the various solvents and thinners employed. It is, therefore, desirable to establish that a coating and the specified thinner are compatible and the reduced material is stable. Hence the suggested diluent should, without excessive stirring or shaking, be readily incorporated into the coating in the recommended proportions or to a specified viscosity. Method 4203 in FTMS No. 141 requires that the mixture be allowed to stand for 4 h and then be observed for curdling, flocculation, precipitation, or separation into layers. If there is doubt about the stability, some of the material is then flowed onto a glass panel where any incompatibility is more evident.

Penetration (Absorption)

This term refers to the tendency of the nonvolatile vehicle or binder in a coating to penetrate and be absorbed by porous surfaces. Good resistance to absorption (hold-out) is desirable with interior primers and undercoats because it enables them to seal such surfaces, thus promoting uniformity in both gloss and color of subsequent finish coats. Conversely, a

high level of penetration is desirable with exterior coatings because it promotes adhesion on substrates that are untreated and have layers of rust or degraded, chalky paint. In general, the binders in solvent-borne architectural coatings tend to penetrate chalk and rust very well owing to their lower molecular weight in comparison to that of latex binders. Since the latter penetrate very poorly, exterior latex paints are sometimes modified with alkyd or oleoresinous binders to bind the chalk layer to the old coating.

Method 4421 of FTMS 141 is a roughly quantitative method for measuring absorption that employs filter paper as a reproducible porous surface. In the test, a friction-top lid for a half-pint can is completely filled with paint and covered with a standard grade filter paper. After 3 h, vehicle migration is observed as a spreading circular stain in the paper, and the mean distance from the rim of the cover is reported as the degree of absorption or penetration. Blotting paper may also be used for this test. Method 6261 of FTMS 141 is a more practical procedure than Method 4421, involving application of the material to an imperfectly primed porous surface and, after drying, observation for variations in gloss and/or color. In the U.S. Federal Specification for Interior Flat Latex Base Paint (TT-P-29) the test paint is applied with an applicator blade to a half-sealed penetration chart, and the above-described differences between the sealed and unsealed areas are measured instrumentally.

Color Compatibility

A colorant sometimes fails to disperse completely and yield the desired color in a white or tint base owing to poor compatibility that can be related to the colorant (color development), the base (color acceptance), or both. If colorants are not adequately compatible with bases, lighter or nonuniform shades are produced. Although the problem is generally related to poor dispersability of the colorant, especially those designed for use with both solvent- and water-reducible coatings, the white pigment in the base may not have been adequately dispersed or may have subsequently flocculated. In that case, if the shear applied to disperse the colorant also disperses the white pigment, the color will be lighter and less colorful (i.e., less saturated) than expected. When both the colorant and the white are poorly dispersed, the color change due to shear stress will be some combination of the two effects.

Poor color compatibility can be a problem both in the production and use of organic coatings. In the factory it causes a loss of monetary value and unpredictable tinting results. In application it results in nonuniform color of the final film due to the variation in shear forces with different modes of application. This is commonly evaluated by applying the coating with an applicator blade and subjecting a small area of the drawdown to high shear by finger rubbing the partially dried film. Since rubbing simulates the high shear involved with some application methods, a variation between the unrubbed and rubbed areas indicates that the product will probably exhibit the same defect in the field. The color difference can be measured photometrically to obtain numerical values that are more useful than visual evaluations for establishing limits for control work. Unfortunately, the finger-rub method has been found to have poor repeatability (same operator, different times) as well as poor reproducibility (different operators).

In ASTM Test Method for Color Development in Tinted Latex Paints (D 5326), a portion of the semi-dry film is subjected to closely controlled brushing for development of a strong shear force. Although the method is written for testing a tinted paint, the basic procedure can be followed for rating how well different colorants perform in the same tint base or vice versa.

Coating Rheology

This term refers to the viscometric characteristics of liquid coatings. Simple liquids that maintain a constant viscosity at varying shear conditions are said to be Newtonian. Most architectural coatings are non-Newtonian in character and have a higher viscosity at low shear rates than at high shear rates and vice versa. Systems of this type require the application of a minimum force to flow and when this force, the "yield value," is exceeded, the phenomenon is called plastic flow. Paints that exhibit plastic flow are called Bingham liquids.

In the coating industry, thixotropy is a favorable form of non-Newtonian flow in which a liquid decreases in viscosity when subjected to a shearing force and then recovers when undisturbed for some time. It is possible for a material to exhibit both plastic flow and thixotropy. These flow characteristics are directly related to practical application properties. High viscosity at low shear rates results in poor leveling and good sag resistance. Low viscosity at moderate shear rates leads to good leveling but poor sag resistance. High viscosity at high shear rates, such as occur during brush application, results in brush drag or poor brushability. Consequently, a balance between the different properties must be sought.

The different instrumental test methods used for coatings are described below. Empirical methods for evaluating various application characteristics are described in a later section. The topics of rheology, viscometry, and related characteristics are dealt with on a theoretical, mathematical basis elsewhere in the manual.

Consistency (Low-Shear Viscosity)

Consistency is a general term that describes the perceived thickness or "body" of liquids and is related to application and flow. While it is related to viscosity, consistency does not distinguish between different viscosity types and does not determine the quality of a coating. It is used mainly to ensure product uniformity and should, therefore, fall within a stated range for satisfactory reproduction of a specific formula. The most common device for measuring the consistency of architectural coatings is the Krebs modification of the Stormer Viscometer in which a small off-set T-shaped paddle is immersed to standard depth in the test fluid and rotated at 200 r/min for instruments with a stroboscopic timer and 200 ± 20 for those without the timer. Weights are varied to obtain the specified shear rate with the greater the load, the higher the consistency that may be expressed in grams/200 r/min or Krebs Units (KU). Although the consistency of most architectural coatings is about 150 to 300 g/100 revolutions (72 to 95 KU), a much wider range is possible because of the great

variation that can occur in the rheological properties of these materials. Two paints of the same consistency may have quite different rheological properties during application. Consistency is determined in accordance with ASTM Test Method for Consistency of Paints Using the Stormer Viscometer (D 562).

Rheological Properties of Non-Newtonian Materials

The two methods covered in this subsection are particularly suited for coatings that display thixotropic characteristics. However, they measure viscosity under different shear rates. In ASTM Test Method for High-Shear Viscosity Using the ICI Cone/Plate Viscometer (D 4287), there is only one very high rate that is similar to that occurring during brush application so that the measured viscosity is related to brush drag, spreading rate, and film build. ASTM Test Method for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield) Viscometer (D 2196) employs a rotational viscometer to measure viscosity at several shear rates to determine the amount of shear thinning and the viscosity change at low shear rates. The results can be used to evaluate sag resistance and leveling ability.

Sag Resistance

Some coatings sag and form curtains before the film sets. Resistance to this type of flow is an important property, particularly for semigloss and gloss finishes, because of the resultant unsightly film appearance. Sag resistance is determined in accordance with ASTM Test Methods for Sag Resistance of Paints Using a Multinotch Applicator (D 4400). In this test, a presheared coating is applied to a test chart with a drawdown applicator that contains a number of different-sized notches to form stripes of the coating. The chart is then hung vertically with the drawdown stripes in a horizontal position. The coating chart is allowed to dry and then examined for sagging characteristics.

Leveling Properties

Leveling is an important property when smooth, uniform surfaces are to be produced because it affects hiding and appearance. Brush marks and imperfections are much more conspicuous in semigloss and gloss finishes than they are in low-gloss materials. ASTM Test Method for Leveling of Paints by Drawdown Method (D 4062) is the most recently developed method for evaluating this property. In it, a series of ridges is produced by applying the film using a serrated rod. After drying, the ridges are compared under a strong oblique light to a numbered series of plastic levelness standards. The results have been shown to correlate well with brush applications.

Package Stability

Since paints normally are not used immediately after manufacture, they must remain stable in the can for some reasonable time. At normal temperatures most architectural coatings can be stored for over a year with little change in properties. However, exposure in uninsulated warehouses or during shipping to high temperatures in summer or, for water-dispersed coatings, to low temperatures in winter may cause unacceptable changes in the products. Another unsatisfactory condition that may occur during storage is excessive settling.

Heat Stability—Exposure to high temperatures can be used as an accelerated test to predict stability of a packaged coating when stored at normal temperatures or to test for the heat stability when a material frequently encounters such conditions in service. Although indications of long-term package stability can usually be obtained in several days or weeks at an elevated temperature such at 125°F (50°C) or 140°F (60°C), occasionally the results of such accelerated tests do not agree with those at prolonged normal storage conditions. In ASTM Test Method for Package Stability of Paint (D 1849), the changes in consistency and certain other properties of the accelerated aged material are compared to those occurring in a control kept at normal temperatures for a longer period. When testing for heat stability, as such, changes in viscosity, flow, gloss, pH, foam resistance, color uniformity, and wet adhesion are usually checked.

Settling—Modern coatings are generally resistant to marked or hard settling, but at times they do exhibit separation and soft settling. The degree of pigment suspension in a shelf-aged specimen and the ease of remixing it to a homogeneous condition suitable for the intended use are determined in accordance with ASTM Test Method for Evaluating Degree of Settling of Paint (D 869).

APPLICATION PROPERTIES

Application or working properties of a coating are generally compared to a standard or described by requirements in the product specification. Working properties are determined in accordance with Method 4541 of FTMS 141.

Brush Application

Brushed films should be smooth and free of seeds and when applied to vertical surfaces they should show no sagging, color streaking, or excessive brush marks. Brush drag should not be excessive, although some degree of drag may be desirable for adequate film thickness application. Wall finishes are tested on vertical surfaces and floor coatings on horizontal surfaces, although evaluation of the latter on vertical surfaces may be necessary to determine performance on stair risers, railings, posts, etc. Brushing properties are determined in accordance with Method 2141 of FTMS 141. Even though the test is subjective, someone experienced in the art can produce quite consistent results, particularly in the evaluation of drag qualities.

Brush Drag

As the brush drag (resistance encountered when applying a coating by brush) increases, any natural tendency of the painter to spread the material too far is reduced. All other factors being constant, increased brush drag results in greater film thickness with consequent improvements in hiding and film durability. Conversely, increasing brush drag too much can cause difficulties in easily and uniformly spreading the coating. This can lead to excessive sagging, prolonged drying time and, in highly pigmented materials, possibly "mud-cracking" due to excessive thickness. The determination of the relative brush drag of a series of coatings applied by brush by the same operator is described in ASTM Test

Method for Comparison of the Brush Drag of Latex Paints (D 4958). When testing a group of coatings, they must all be of the same type—all water-borne or solvent-borne. It has been established that the subjective ratings thus obtained correlate well with high-shear viscosities obtained instrumentally using ASTM D 4287 (see above), provided the materials differ in viscosity by at least 0.3 P (0.03 Pa·s).

Roller Application

Both wall and floor coatings are frequently applied by roller. This type of application tends to produce some stipple pattern. The evaluation of a material's characteristics when applied by roller is covered by Method 2112 of FTMS 141. Since foaming often occurs when water-borne coatings are roller applied, the amount of foam produced and the number of craters that remain after the bubbles have broken should be determined during the test.

Roller Spatter—Some coatings spatter more than others when applied by roller. The degree to which a material spatters when roller applied can be determined by the density of the spatter. In ASTM Test Method for Measurement of Paint Spatter Resistance to Roller Application (D 4707) a specially designed notched spool is rolled through a film of the test material that has been applied to a plastic panel. Any spatter generated falls on a catch paper and after drying is rated against photographic standards. This procedure eliminates the influence of the roller cover, thus determining the spattering characteristics of the material alone.

Spray Application

Architectural coatings are some times applied by spray. Both air and airless spray are used on commercial work. Spray application properties are determined in accordance with Method 2131 of FTMS 141. Manual application is very subjective and should be performed only by an individual skilled in the art of using spray equipment.

Touch-Up Uniformity

After a paint has dried, areas where less material was applied sometimes become noticeable. If the paint has suitable touch-up properties, additional material can be applied to these areas only, instead of refinishing the complete object—wall, side of building, etc. The color, gloss, and leveling of the touched-up areas and the previously coated area should be uniform. Differences in these properties are often caused by short wet-edge time, poor leveling on recoat, and pigment orientation or flotation during and after application. Touch-up properties are determined in accordance with ASTM Test Method for Evaluation of Gloss or Sheen Uniformity (D 3928).

APPEARANCE OF THE DRY FILM

Specimens for evaluating appearance properties should conform to ASTM Practice for Selection of Coating Specimens for Appearance Measurements (D 3964).

Color

The appearance of color is greatly influenced by several factors. A color next to a yellow wall looks different than the same color next to a blue wall. The visual appearance of a colored object illuminated by incandescent light, fluorescent light, and natural light differs because the spectral composition of the different incident light sources varies. Gloss also affects color appearance. The same color in a low-gloss finish usually appears to differ when in a high-gloss coating even though instrumentally the colors may be identical. A more theoretical discussion of optical characteristics of coatings appears elsewhere in the manual.

Color Differences by Visual Comparison

Visual comparison of colors is fast and often acceptable even though numerical values are not obtained. ASTM Practice for Visual Evaluation of Color Differences of Opaque Materials (D 1729) covers the spectral, photometric, and geometric characteristics of light source, illuminating and viewing conditions, sizes of specimens, and general procedures to be used in the visual evaluation of color differences of opaque materials relative to their standards.

Color Differences Using Instrumental Measurements

The difference in color between a product and its standard can be measured by instrument. Generally the tolerance is agreed on by the purchaser and seller and may also be required if a product specification is involved. Color measuring instruments provide numerical values that can be compared to subsequent measurements. ASTM Test Method for Calculation of Color Differences from Instrumentally Measured Color Coordinates (D 2244) describes calculation of the small color differences observable in daylight illumination between nonfluorescent, nonmetameric, opaque surfaces such as coated specimens. If metamerism is suspected, visual evaluation should be used to verify the results.

Directional Reflectance

This property is a measure of the appearance of lightness of a coating. It is usually assigned a value in specifications for white and pastel shades with a typical range of 76 to 86% for white finishes. In ASTM Test Method for Color and Color Difference Measurement by Tristimulis (Filter) Colorimetry (E 1347), the directions of illumination and viewing are specified so the effect of gloss on the reflectance determination is eliminated.

Gloss

Gloss is a measure of the capability of a coating surface to reflect light in a mirror-like (specular) manner, i.e., light strikes the surface and is reflected at the equal but opposite angle. In ASTM Test Method for Specular Gloss (D 523), the numerical gloss units are the ratio of light reflected by a specimen to that reflected by the standard black glass that is assigned a gloss value of 100. The gloss of some coatings

varies greatly with the angle of incidence, so that a complete description of their gloss would require measurements to be made over a wide range of angles. In practice, the gloss of architectural finishes is adequately characterized by measurements at 60 or 85° (or both) from a line perpendicular (normal) to the surface. The 85° angle is a very low angle of illumination (a "grazing" angle of 5°) and viewing the surface and gloss at this angle is called "sheen." Attempts to standardize the levels of gloss associated with various descriptive gloss terms have not been very successful since the gloss scale is continuous with no distinct boundaries. Hence, there is considerable overlap among the gloss classifications in common usage.

Gloss, 60°

Semigloss enamels are particularly sensitive to poor enamel hold-out of primers and undercoats. Low or uneven gloss readings are indicative of this defect. Oil and alkyd house paints typically have values of 30 to 70 while trim enamels have values of 70 to 90 for 60° gloss. Floor enamels generally have a high (90+) gloss reading when first applied, but this decreases with time and traffic. Interior semigloss enamels after drying 48 h are usually in the range of 40 to 70, but measurements taken shortly after drying should be repeated after one week because the gloss can decrease significantly in the first few days of drying.

Sheen, 85° Gloss

Although low-gloss paints with good uniformity of appearance at low viewing angles often have little sheen and those with good cleansability usually have moderate sheen, this is not always the case so that sheen should not be used as a measure of other paint properties. ASTM D 523 is useful for characterizing the low-angle appearance of low-gloss coatings when the 85° geometry is employed. Most flat wall paints have a sheen of about 1 to 10 whereas velvets or eggshells range from 15 to 35.

Hiding Power

An in-depth discussion of this appearance property can be found elsewhere in the manual, so this section only briefly reviews the commonly used test methods. ASTM Test Method for Hiding Power of Paints by Reflectometry (D 2805) is precise and gives an absolute rather than a comparative result. The coating is applied with a blade-type applicator to minimize the effects of flow and leveling. Film thickness is precisely measured and film opacity is instrumentally determined. ASTM Test Method for Relative Hiding Power of Paints by Visual Evaluation of Brushouts (D 344) is a more practical test in which paint is applied with a brush on a checkerboard chart, wet-film thickness is approximately controlled by spreading rate, and hiding power is visually evaluated by comparison with a standard paint. However, results are affected by the flow and leveling of the paint. ASTM Test Method for Hiding Power of Architectural Paints Applied by Roller (D 5150) is designed to simulate application with the common tools. Although other tools may be used, the method describes use of a roller to coat a 6-ft^2 (0.56-m^2) chart printed with a series of gray stripes. The test is intended to demonstrate the hiding obtainable when the coatings are applied by experienced workers.

PROPERTIES OF THE DRY FILM

Interior and Exterior Coatings

Abrasion Resistance

This characteristic is a measure of the ability of a dried film to withstand wear from foot traffic and marring from objects rolled or pulled across the surface. Dry abrasion resistance is determined in accordance with ASTM Test Method for Abrasion Resistance of Organic Coatings by Air Blast Abrasive (D 658), ASTM Test Method for Abrasion Resistance of Organic Coatings by Falling Abrasive (D 968), and ASTM Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser (D 4060). In these methods, dry abrasive is applied to a coated panel using a jet blast (D 658) or the force of gravity (D 968) when the abrasives are free flowing. In the case of the Taber test, a weighted wheel that has abrasive embedded in a resilient rubber matrix is used. Because of the poor reproducibility of abrasion methods, testing should be restricted to only one laboratory when numerical abrasion resistance values are to be used. Interlaboratory agreement is improved significantly when rankings are used in place of numerical values.

Adhesion

The ability of a film to resist removal from a substrate is certainly an important coating property. It is evaluated by many different procedures, almost all of which are not completely satisfactory because the removal force is not applied at the coating-substrate interface but at the coating surface. Consequently, when the adhesive bond between coating and substrate is greater than the cohesive strength of the coating, failure occurs within the film, so that adhesion, per se, is not measured. When multicoat systems are involved, the failure can also be between coats. Nevertheless, the tests are used to estimate whether the adhesion is adequate for the intended service.

The test most commonly used with coatings is ASTM Test Methods for Measuring Adhesion by Tape Test (D 3359). In it, a simple procedure for use in the field comprises cutting an X in the film, applying pressure-sensitive tape over the cut, removing the tape, and qualitatively assessing adhesion on a zero to five scale. The more quantitative procedure involves making a six- or eleven-cut lattice in the film. After applying and removing the tape, coating removal is evaluated by comparison with a scale that is related to the estimated area of removal. If a tool that makes all cuts in one direction is available, the test can be made in the field. However, when individual cuts are made using a metal cutting guide, the test is practical only for laboratory use. Since the cuts must be made through the coating to the substrate, the latter must be sufficiently hard to resist the cutting tool. Consequently, the test is not applicable on soft substrates such as wood, plastic, or wallboard [*3*].

Another laboratory method that requires a relatively hard substrate is ASTM Test Method for Adhesion of Organic Coatings by Scrape Adhesion (D 2197). In this method,

coated test panels are pushed beneath a rounded metal loop that is loaded with increasing weight until the coating is removed. The advantage of this procedure is that the results are numerical. Its limitation is that coatings with very good adhesion, such as coil-coated substrates, require loads of up to 10 kg. Thus, it is difficult to push panels under the loaded loop without causing it to skip along the coating surface.

ASTM Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers (D 4541) also provides numerical results. The procedure comprises adhering a metal stud to the coating surface with an adhesive, curing the latter, attaching the test apparatus to the stud, and applying a perpendicular force that is increased until either the coating is detached, a specified value is reached, or the adhesive fails. While the hardness of the substrate is not a factor, its cohesive strength is important. As a result, failure can occur within the substrate, the coating, or the adhesive, or at the stud-adhesive interface, the adhesive-coating interface, or even the coating-substrate interface. As indicated by the title, the testers are designed for use in the field. They can, however, be used in the laboratory unless the adhesive bond strength is very high. In this case, a tensile testing apparatus and high-strength adhesive are required.

Wet Adhesion

It is essential that a finish tightly adhere to a given substrate or primer under the wet conditions of washing or scrubbing. The wet adhesion procedure described in Method 6301 of FTMS 141 is essentially an earlier version of Method A of ASTM D 3359. In it, two parallel cuts are made 1 in. (25 mm) apart instead of the X-cut. Then masking tape, which changes markedly in adhesiveness with time, is pressed against the coating surface with a roller instead of semitransparent tape being rubbed with a pencil eraser. In this method, the water immersion prior to testing is described in detail instead of being referred to in a Note.

Flexibility

Elongation is a measure of a coating's flexibility. Most semigloss and full gloss coatings can be bent over a ⅛-in. (3.2-mm) mandrel without affecting the film. However, interior flat and eggshell water-borne finishes usually pass at ¼ in. (6.4 mm), while solvent-borne coatings of the same category may pass only a ½-in. (12.7-mm) bend. Flexibility of interior coatings is usually evaluated using one of the mandrel procedures in ASTM Test Methods for Mandrel Bend Test of Attached Organic Coatings (D 522). However, measuring elongation directly with a tensile testing machine as described in ASTM Test Method for Tensile Properties of Organic Coatings (D 2370) is a much more discriminating way of estimating the flexibility retention of exterior coatings [*4*].

Resistance to Household Chemicals

An important property of some finishes is their ability to resist discoloration, spotting, softening, blistering, or removal when subjected to household chemicals or strong cleaners. In ASTM Test Method for Effect of Household Chemicals on Clear and Pigmented Organic Finishes (D 1308), the resistance may be evaluated with household items ranging from cold water, to detergent solutions, to staining materials such as mustard. The test may be run as covered or uncovered drops applied to horizontal plane surfaces or by immersing panels in the relevant fluids.

Interior Finishes

Block Resistance

This is an important property for interior semigloss and gloss finishes since it governs the resistance of dried coating surfaces to sticking together when stacked or placed in contact with each other. An interior finish often comes in contact with itself, especially on doors, windows, and drawers where it sometimes adheres to itself. Such blocking is dependent on the hardness of the coating and the applied pressure, temperature, humidity, and time while the surfaces are in contact. ASTM Test Method for Blocking Resistance of Architectural Paints (D 4946) covers an accelerated blocking-resistance procedure especially developed for this type coating.

Print Resistance

The ability of a coating to resist printing is important because its appearance is adversely affected if the surface texture is modified by contact with another surface, particularly one with a pattern. Interior gloss and semigloss systems applied to window sills and other horizontal surfaces are often loaded with flower pots and similar objects that tend to leave a permanent impression from the applied pressure. The tendency for a film to "print" is often a function of the hardness of the coating and the applied pressure, humidity, and time while the surfaces are in contact. In ASTM Test Method for Print Resistance of Architectural Paints (D 2064), the resistance is evaluated by placing a piece of four-ply cheesecloth on a coated glass slide, and a 500-g weight on a rubber stopper are added to create pressure. The test is accelerated by placing the assembly in an oven at 140°F (60°C) for an hour. After cooling, the film is subjectively rated for the degree of imprinting.

Film Porosity

The more porous a coating, the worse are its cleansability and enamel holdout. In ASTM Test Method for Porosity of Paint Films (D 3258), a special, colored penetrating medium is applied to the coating and the change in reflectance indicates the degree of porosity.

Washability and Cleansability

The capability of satisfactorily removing marks without damaging the film is essential for good performance of interior finishes. A coating may be washable, that is, unaffected by the detergent solution, but may not have good cleansability. Washability is evaluated by determining the resistance of the film to wet erosion either by visual assessment or measured film loss. Cleansability is evaluated by applying one or more stains and soils and determining how readily they are removed. Frequently the difference between the two terms, "cleansability" and "washability," is not clearly understood so that there is confusion as to what is really being tested [*5*]. For example, the title of ASTM D 3450 is Test Method for Washability [sic] Properties of Interior Architectural Coatings, while the method's Scope states that it is designed for determining "ease of removal of soilant." In general, the pre-

cision of both types of test is poor because several properties, such as hardness, water and detergent resistance, cohesion, and adhesion, are involved, and the end-point, except for the wet abrasion method, is rather indefinite.

Washability

This parameter is also referred to as "resistance to scrubbing" or "resistance to wet abrasion." ASTM Test Method for Scrub Resistance of Interior Latex Flat Wall Paints (D 2486) was developed for interior latex flat wall paints but can be applied to coatings of almost any type. In the test, the coating is applied to a black plastic panel that, during scrubbing with a nylon brush and abrasive cleaning agent, is raised by a narrow shim to concentrate the test area. The number of back-and-forth strokes (cycles) required to remove the film over the shim is determined. Interior latex low-gloss finishes can vary in scrub resistance from less than 100 to more than 1000 cycles.

ASTM Test Method for Wet Abrasion Resistance of Interior Paints (D 4213) is similar except that a sponge is used in place of the bristle brush and the shim is not used. In the original method, the loss per 100 cycles to erode the film almost to exposure of the black substrate was calculated on the basis of either weight or volume. In the current method weight was eliminated, even though it is easier to determine, because volume characteristics, such as pigment volume content, usually have a more direct relation to performance, which in this case is scrub resistance or washability.

Cleansability

The older of the methods for this type measurement, ASTM D 3450, is similar to the wet-abrasion method, ASTM D 4213, except a sponge is used with either the nonabrasive or abrasive cleaning agent to remove a carbon black-oil stain. The ability to remove the stain is expressed as the ratio (in relative percent) of the reflectance of the cleaned area to that of the area before application of the stain. In ASTM Test Method for Practical Washability [sic] of Organic Coatings (D 4828), numerous staining and soiling agents found in service, and commercial abrasive or nonabrasive cleansers, as well as the standardized cleaning agents, can be used. In the revised edition, the film may be cleansed manually or mechanically, but only the latter is suitable for interlaboratory testing.

Exterior Coatings

Adhesion to Chalky Surfaces

Latex paints generally have little ability to penetrate powdery substrates. Consequently, adhesion to previous coatings that have chalked is poor unless the latex paint has been modified to penetrate and bind the chalk layer to the old coating. However, certain latexes do exist that are designed to adhere well to chalky surfaces and thus do not require modification. At the time of writing, there are no ASTM test methods for adhesion to chalky surfaces, although work toward development of such a test is proceeding. The industry generally uses a pressure-sensitive tape to test for this property. The tape is pressed firmly onto the dried latex film (fresh films do not adhere as well as aged, dried films) and then removed rapidly by pulling back on itself. Method 6301 of FSTM 141 describes a similar method but it includes water exposure.

Dirt Pickup

Low-gloss exterior latex paints generally have good resistance to dirt pickup, but gloss or semigloss latex paints may be more subject to this type of disfigurement. Exterior exposure, particularly under an overhang (soffit), should indicate in a relatively short time (about one year) a paint's tendency to collect dirt when evaluated in accordance with ASTM Test Method for Quantifying Dirt Collection on Coated Exterior Panels (D 3719).

Fume Resistance

Some paints undergo a change in appearance, usually color, when subjected to air containing certain sulfur compounds, notably hydrogen sulfide and sulfur dioxide. This type of atmosphere may be present near industrial or other polluted areas and can cause a paint to yellow or darken in as little time as overnight. At the time of writing, no ASTM or federal test methods are available for evaluating this color change, but one procedure used by the industry is as follows: Apply a sufficient number of coats of the paint to two glass plates to hide completely the glass surface and allow to dry for 6 h. Then expose one plate in a moist atmosphere of hydrogen sulfide for 18 h. Compare the color of the exposed film with that of the unexposed one. The color difference should not exceed that which exists between two plates coated with a paint made with titanium dioxide pigment, lead-free zinc oxide, raw or refined linseed oil, and sufficient cobalt added for drying purposes, and similarly treated.

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[1] *Paint/Coatings Dictionary,* Stanley LeSota, ed., Federation of Societies for Coating Technology, Blue Bell, PA 19422, 1978.

[2] Brezinski, J. J., *Manual on Determination of Volatile Organic Compounds in Paints, Inks, and Related Coating Products, ASTM MNL 4,* 2d ed., ASTM, Philadelphia, PA 19103, 1993.

[3] For more information about the tape test, see Commentary in the Appendix to ASTM D 3359.

[4] Ashton, H. E., "Flexibility and its Retention in Clear Coatings Exposed to Weathering," *Journal of Coatings Technology,* Vol. 51, No. 653, June 1979, p. 41.

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Artists' Paints

by Benjamin Gavett[1]

AS COATINGS, ARTISTS' PAINTS ARE DECORATIVE IN NATURE and are usually intended to endure for decades or centuries under conditions of indoor storage and display. Relative to other coatings, they are highly loaded, most often with a single pigment. Thickness of application ranges from transparent washes to thick, textural builds. Typical tools used include the airbrush, paintbrush, and palette knife, but paints are also often applied by other means, such as rags, sponges, or with the hands. They are often modified at the time of application to change sheen, texture, color, flow, or other characteristics. The substrate used is usually paper or a cotton or linen duck stretched over an open frame, but may be almost anything else, including solid or compressed wood panels, paperboard, metal, synthetic fabric, glass, figurines, clothing, or walls.

Artists' paints are categorized according to their vehicle or binder. Most common are oil (alkali-refined linseed oil), acrylic (acrylic emulsion), and water color (gum arabic). Variations of these include cold-pressed linseed oil, other drying oils of vegetable origin, and acrylic emulsion copolymers. Other natural and synthetic materials of historic significance or which are in more limited current use are acrylic solution, polyvinyl acetate, casein, egg, wax, and various gums.

Although almost any paint will be used by an artist, those formulated for such use are expected, above all else, to be as permanent as possible. However, paint is only one element in the process of manipulating materials to transform vision and ideas into art. Stability of the finished work is a function not only of the paint used, but also of application technique, substrate, age, storage, handling, and ambient environmental conditions.

TESTING OF ARTISTS' PAINTS

Testing of artists' paints is done to ensure quality and consistency in their manufacture and to establish performance parameters such as flexibility, durability, or adhesion to various substrates. Some performance criteria, such as lightfastness, are similar among different types of paints. Others can be quite different, such as flexibility and drying time of oil paints versus acrylics. It is up to the manufacturer to perform tests necessary to ensure that the paints are of a quality consistent with or exceeding that which is expected and historically true for the type of paint being produced. The artist, through experience and education, must be aware of the particular limitations inherent with each type of paint. When new applications are explored, as is often the case with art, it becomes necessary to select and perform tests which will provide confidence that the finished artwork will have the desired physical integrity.

The tests described in this section have been found to be useful to quantitatively and qualitatively describe various characteristics of artists' paints. Acceptability of quality is determined between buyer and seller. In practice, it is largely dependent upon what is considered characteristic of the particular paint type. Many of these test methods are ASTM standards that the reader should consult for further details. It is important to note that there are ASTM standard specifications for several types of artists' paints, including acrylic emulsion, watercolor, oil, resin-oil, and alkyd. These represent the current consensus, between producers, consumers, and other interested parties, of minimally acceptable performance characteristics and other criteria. Most of the following test methods were not developed for artist paints in particular. Due to the wide spectrum of types of artists' paints and potential uses, this listing does not include all test methods that may be relevant. Those included are of varying importance and applicability. They are in alphabetical order, grouped loosely into several categories: Shelf Stability, Working Properties, Film Properties, and Safety and Compliance.

Shelf Stability

It is common for art materials to languish for years on store shelves prior to being purchased. Once purchased, a container is typically opened and closed many times during a life cycle which may take months or years. Stability is evaluated to help ensure endurance of the product through foreseeable conditions of storage and use.

Appearance

The appearance of the undisturbed paint in the container creates an impression of quality, regardless of the ease of restoring it to a homogenous condition. Evaluations for appearance in the retail container are most accurate when based on true conditions of storage and use. However, this is not practical when developing new products. Potential failure may be more quickly realized by placing samples in a laboratory oven at moderately elevated temperature. As the difference between normal and test temperature increases, accuracy in predicting potential problems may decrease because higher temperatures may exaggerate changes. In a study of

[1]Assistant technical director, Golden Artist Colors, Inc., Bell Road, New Berlin, NY 13411.

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latex paints published in the *Journal of Coatings Technology* [*1*], the authors concluded that an oven temperature of approximately 50°C most accurately predicted shelf life performance. Items to note regarding appearance may include skinning, surface cracking, or separation. Parameters of acceptability will vary depending upon expectations of the customer for the particular type of paint.

Color Change

Sometimes the color of a paint film produced from a container of paint changes during storage, for example, as can happen when a pigment is not compatible with the pH of the formulation. This may be determined by preparing a fresh batch of the paint to be tested and immediately preparing a drawdown from it. Subsequent drawdowns at the same thickness may be periodically prepared from the same batch after the paint has aged in the container. The subsequent drawdowns are compared against the original. The results obtained from this test may be accelerated by using a laboratory oven.

Consistency

During storage and use, it is desirable that the paints maintain their intended texture and body. Evaluations are based on visual observation and workability with typical application tools. Items to note include mealiness, tackiness, elongation, and break, as well as other body characteristics. Conclusions may be drawn by comparing batches of the same formula, made at different times, which have been stored and otherwise treated similarly. It is useful to evaluate both full and partially empty containers.

Flocculation

To determine if the pigment is fully dispersed or has remained dispersed over time, a tint of the color is prepared with a compatible white. A drawdown is made and the excess paint is recovered and set aside until the drawdown is dry. Next, a small amount of the original wet mixture is placed on top of the dried paint film. This paint is then rubbed under pressure in a circular motion (a gloved thumb is suitable) in an effort to cause further dispersion of the pigment. If it has become more fully dispersed, the rubbed paint will appear as a stronger tint against the original drawdown.

Freeze-Thaw Stability

Shipping and storage often expose artists' paints to extreme temperature fluctuations. Water-based paints can be quickly ruined if not formulated for protection from freezing. ASTM Specification for Artists' Acrylic Emulsion Paints (D 5098), in Section 6.10 of the *ASTM Book of Standards*, describes the procedure used for testing acrylic paints. The same procedure is used for watercolors. To meet the requirements of the standard, the paints must pass five freeze-thaw cycles while retaining proper consistency.

Package Integrity

The expected life and use of the package containing the paints should be considered when designing appropriate tests. Consider, for example, how the container will be shipped or how many times a tube will be flexed. Potential interactions between the paint and packaging should also be evaluated. For example, solvents may migrate through the walls of plastic containers, causing them to become drawn inward. Real time evaluations are best, but potential failure can be accelerated by increasing temperature or solvent load.

Seeding

Paint ingredient incompatibilities may result in the formation of agglomerates. This can be readily observed by preparing drawdowns of the paint, as described in ASTM Practice for Preparing Drawdowns of Artists' Paste Paint (D 4941) and examining the dried paint film. ASTM Test Methods for Coarse Particles in Pigments, Pastes, and Paints (D 185) may also be used.

Settling

In low-viscosity formulations, it is common for pigments to exhibit some settling. Ideally this would not happen, but if it does, it is important that the pigments are easily remixed. Settling that occurs over time may be evaluated according to ASTM Test Method for Evaluating Degree of Settling of Paint (D 869).

Spoilage/Putrefaction

It is necessary to protect against microbial contamination from raw materials and packaging or that may be introduced during manufacturing. Also, since artists' paints are typically opened, used, and reclosed many times, it is important that they be formulated to resist microbial growth from contamination occurring subsequent to purchase by the consumer. ANSI Z356.5, American National Standard for Art and Craft Materials-Paints and Inks, Section 4.2, describes a test method for evaluating the effectiveness of preservatives used in paint formulations. Paints to be tested are inoculated with pieces of bread which have been covered with a sugar solution and allowed to mold. After two weeks, the paints are inspected for decomposition.

Viscosity Changes

Paint stability is quickly and quantitatively evaluated by monitoring viscosity. Viscometer type and method have not been standardized for artists' paints. If needed, a method may be agreed upon between buyer and seller. For most purposes, it is sufficient to ensure consistency of test conditions and equipment when doing periodic rechecks. Accelerated aging with the use of a laboratory oven is usually predictable of real-time viscosity stability of water-based paints.

Working Properties

Many attributes of importance to the consumer of artists' paints are difficult to measure and report with repeatability. This subjectivity is often coupled with varying preferences among users. An ideal paint for one artist may be lacking in certain qualities for the next. It is not as important to standardize these characteristics as it is to determine them and transfer this knowledge to the buyer.

Brushing Characteristics

Paints are brushed out on standard substrates by experienced technicians and rated as being smooth, sticky, tacky, or fluid, as described in Section 6.6 of Commercial Standard

(CS98) for Artists' Oil Paints [2]. This was the original quality standard for artists' paints and was the base from which the subsequent ASTM artists' paint quality standards were developed. It is also common to describe artists' paints for their tendency to flow and level or hold brush strokes and peaks.

Color Variation

If constancy of color is desired, it may be determined by placing samples next to each other on a test card and drawing them down together using a thin film applicator. Comparisons of masstone, undertone, and tint are useful. For quantification and reporting, spectrophotometric measurements and C.I.E. L*a*b* color difference may be obtained according to the practices described in ASTM Test Method for Calculation of Color Differences from Instrumentally Measured Color Coordinates (D 2244).

Drying Time

ASTM D 5098, for acrylics, and ASTM Specification for Artists' Oil, Resin-Oil, and Alkyd Paints (D 4302), specify drying time requirements. Dust-free drying time of these and other types of paints are determined by following the procedures described in ASTM Test Methods for Drying, Curing, or Film Formation of Organic Coatings at Room Temperature (D 1640).

Fineness of Dispersion

Finely dispersed pigments are important for smooth brushing, realizing tinting strength potential, and maximizing encapsulation of pigment within the binder. ASTM Test Method for Fineness of Dispersion of Pigment-Vehicle Systems (D 1210) may be followed to measure this characteristic.

Odor

Evaluation of odor may be important in determining potential consumer acceptance of artists' paints. The different vehicles have characteristic odors and what is objectionable to some may not be to others. Formula variations may be rated, based on the acceptability of their odor, by a panel of intended users.

Opacity

Opacity is not standardized for artists' paints. It is expected to vary depending on the pigment and vehicle used. The artist benefits if opacity ratings are reported on the container or in manufacturers' literature. This characteristic is typically evaluated by applying a drawdown over a test panel that has adjoining areas of black and white. A scale is then established and colors are assigned values relating to a range from highly transparent to fully opaque.

Tinting Strength

The potency of a color is indicative of its value to the user, particularly when blending with white (absorption tinting strength). Depending on chemical composition, pigments are expected to vary accordingly in strength. Identically pigmented paints may exhibit differences due to degree of processing or loading. It would not be appropriate to critically compare paints of different vehicles because of differences in the loads they will tolerate. ASTM Standard Test Method for Determining the Relative Tinting Strength of Chromatic Paints (D 4838) may be followed to arrive at instrumentally derived determinations of tinting strength relative to that of a standard or reference paint. Simple comparisons between paints can be made by using a white paint of standard composition and strength to prepare tints, which are then drawn down along side of each other. The tints are most accurately prepared using a weight-based ratio of the standard white to the test color. A ratio based on volume, using syringes, may be useful if an accurate balance is not available or if it otherwise suits the purpose of the user.

Viscosity

Artists' paints are available in a wide range of viscosities, from pourable ink-like to heavy impasto. Oil paints are typically expected to maintain definition of the brush stroke, provide sharp peaks, and retain their shape as they emerge from the tube. Water-based vehicles are highly manipulative, and the desired viscosity is dependent on the intentions of the user and manufacturer. Viscosity, thixotropy, and dilatancy may be determined with the equipment and techniques described in ASTM Test Methods for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield) Viscometer (D 2196).

Film Properties

Adhesion

Intercoat and substrate bonding of artists' paints are extremely important. They become especially critical to evaluate when determining surface preparation techniques for new or unusual substrates or when considering multi-media applications. There are many types of adhesion testing apparatuses, but a useful and inexpensive test involves cutting the paint films and attempting to lift them with pressure-sensitive tape. This is described in ASTM Test Methods for Measuring Adhesion by Tape Test (D 3359).

Bleeding

Artists' paintings are typically created in a manner that results in overlapped or layered films. The tendency for color of an underlying dry paint film to migrate through to subsequently applied paint is an occasional but usually unwelcome occurrence resulting from the pigment exhibiting some solubility in the vehicle. The tendency for bleeding may be determined by applying an opaque white overstripe onto a smooth, dried paint film. The white is extended off the paint film and onto the uncoated portion of the test support. Discoloration due to bleeding will be readily apparent. This test is described as Test Method B of ASTM Test Methods for Bleeding of Pigments (D 279).

Block Resistance

Artists' paintings are not typically produced, used, or stored in a manner which will cause them to come into contact with and stick to other surfaces. However, there are times when this does occur, such as in production situations or when there is inadequate storage space. If block resistance is important to the user, the paint in question should be evaluated because many artists' paints exhibit inherently poor block resistance. A case-specific test should be designed to simulate worst case scenarios of pressure, temperature, and humidity

fluctuations. Anticipated drying and storage times should also be considered in the test design.

Chemical Resistance

Resistance to the various liquids which a painting may be expected to come into contact with is an important characteristic. These include varnish vehicles, solvents used in varnish removal, and cleaning solutions that may be used on the paint film. Chemicals to be tested with a particular paint vary depending on the type of paint and what is expected of it. A procedure for designing appropriate tests may be based upon the Spot and Immersion Tests described in ASTM Test Method for Effect of Household Chemicals on Clear and Pigmented Organic Finishes (D 1308).

Flexibility

Paints applied to flexible supports, such as stretched cotton or linen canvas, may be susceptible to potentially destructive forces. The different types of artists' paints vary in the degree they will flex without failure. Although there are no established standards, they have different thresholds of expectation and, therefore, acceptability.

During storage or shipping, paintings are often rolled up. ASTM Test Methods for Mandrel Bend Test of Attached Organic Coatings (D 522) describes equipment and methods for determining and rating flexibility. Relevancy is increased by testing the coatings over the intended substrate and primer. Combined with the use of accelerated aging techniques, the mandrel test will help predict natural embrittlement of the paint film.

Paintings must also endure expansion and contraction of the fabric due to changes in environmental humidity and temperature. Sometimes these conditions become extreme, as when a painting is shipped during freezing weather. Failure will occur more quickly if the individual components of the painting have greater relative differences in their moduli of elasticity. Use of a temperature and humidity-controlled environmental chamber programmed to expose paintings to repeated cycles of extreme conditions will accelerate the failure that might be observed over time under normal conditions.

Another force of concern is mechanical impact against the film that may occur during handling. For example, when a painting is mounted on an open-back stretcher, fingers may inadvertently press into it as it is being carried. The risk of damage increases as temperature decreases and the glass transition temperature is approached. The rate at which external forces are applied also influences susceptibility to damage.

Gloss

Some manufacturers of artists' paints will add inert flatting agents to control the gloss values of the various colors so that they are similar within a line. Others will allow a color's gloss to be dictated by the characteristics of the colorant, i.e., tolerable load and particle size. Gloss values for artists' paints have not been standardized. It is a matter of preference and manufacturing philosophy. When required, gloss may be specified between the buyer and seller, with measuring parameters identified.

Lightfastness

ASTM Test Methods for Lightfastness of Pigments Used in Artists' Paints (D 4303) describes three methods used to determine resistance to fading of acrylic, watercolor, alkyd, and resin-oil artists' paints. Included are conditions of exterior exposure under glass, artificial daylight fluorescent lamps, and xenon-arc apparatus. Prior to exposure, samples to be tested are tinted with white until they reach 35 to 45% reflectance at their wavelength of maximum absorption, between 420 and 620 nm. With each method, exposure is continued until specimens have been exposed to a total radiant dose of 1260 MJ/m^2. To meet the ASTM standard specifications for use in artists' paints, the pigments must be tested under at least two of the three methods and exhibit a mean color change of less than eight color difference units (CIE 1976 L*a*b* color difference equation). These test methods are designed to predict performance of artists' paints displayed in typical household or museum environments. Results may not be indicative of performance if the intended use is more rigorous, such as in exterior mural applications.

The most recently developed ASTM practices for determining the lightfastness of artists' materials uses a method of exposing samples indoors to sunlight filtered through window glass while simultaneously exposing a series of eight ISO Blue Wool Reference materials to control the duration of exposure. One half of each specimen and control is shielded from exposure during the test. This test takes longer to run, but it is relatively inexpensive. It is intended for artists' materials which are not specifically covered by other ASTM standard test methods. For details, see ASTM Standard Practice for the Visual Determination of the Lightfastness of Art Materials by the User (D 5398) and ASTM Standard Practice for the Visual Determination of the Lightfastness of Art Materials by Art Technologists (D 5383).

Yellowing

While traditional paint vehicles may be expected to yellow to some degree, this may be considered a serious flaw if encountered in the newer generation of synthetic media. To determine the relative potential for yellowing of a vehicle, a standard titanium dioxide white pigment may be formulated into the test vehicle and into one of known stability. They are then exposed to the accelerated methods described in ASTM D 4303 and amount of yellowing determined with ASTM Practice for Visual Evaluation of Color Differences of Opaque Materials (D 1729) or Test Method D 2244. It is also useful to subject films of the unpigmented vehicles to the same tests.

Safety and Compliance

Flash Point

Solvent-based paints may require flash point determination for label warnings and to determine applicability of shipping regulations. The prescribed test method can vary depending on the authority. ASTM Test Methods for Flash Point of Liquids by Setaflash-Closed-Cup Apparatus (D 3278) is usually applicable.

Toxicological Evaluation

The Federal Hazardous Substances Act (FHSA) requires all art materials to be evaluated by a board-certified toxicologist for potential to cause acute and chronic health effects. This law was incorporated into the FHSA with the Labeling of Hazardous Art Materials Act (LHAMA), the basis of which is ASTM Practice for Labeling Art Materials for Chronic Health Hazards (D 4236). A wide assortment of test methods provide the information required for the toxicological assessment. These are not specified by the Standard Practice or LHAMA, but include all which are embodied in the field of toxicology as well as compositional analysis of the paints and their constituents. For example, test procedures described in EN-71-3:1988, Safety of Toys, are used to determine solubility of metals present in paint, under conditions intended to simulate 4 h in the human alimentary tract. In vitro techniques are also used for determining potential eye and skin irritation. The toxicologist determines any testing that may be required to supplement the information that exists for the raw materials in a product. Appropriate precautionary label information is then assigned. The toxicologist must supply the criteria used in making these determinations to the Consumer Product Safety Commission, the enforcement agency of the Federal Hazardous Substances Act.

Volatile Organic Compounds (VOC)

Artists' paints are sometimes applied to substrates that are covered by VOC regulations. Architectural, sign-painting, and furniture application are examples. ASTM Practice for Calculating Formulation Physical Constants for Paints and Coatings (D 5201) provides equations to calculate the theoretical VOC content of paints, based on the formula and exclusive of water and exempt solvents.

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Automotive Product Tests

by Rose A. Ryntz[1]

EACH OF THE MAJOR AUTOMOTIVE COMPANIES requires a specific protocol of testing to be performed on appropriate substrates in order to grant approval of a particular paint or coating. The specification testing is rigorous and often takes up to two years to complete. This section attempts to provide the reader with a general guideline of the required test methods utilized by the big three automotive companies (GM, Ford, and Chrysler) and where applicable relates to testing required by a Japanese counterpart, Toyota, in gaining materials and processes approval.

AUTOMOTIVE PRODUCT IDENTIFICATION

The approval process at the automotive manufacturers is subdivided into specific categories based on the substrate to be coated, i.e., flexible or rigid, and the coating type tested, i.e., cleaner, primer, topcoat. The outdoor durability of the coating is also a consideration, being designated as a weatherable [good resistance to ultraviolet (UV) degradation] or a nonweatherable (poor resistance to UV degradation) quality.

Surface Cleaners and Pretreatments

Surface cleaners are generally defined as waterborne or solventborne materials that pretreat a substrate prior to the coating process to ensure optimal wetting of the surface. The pretreatment then renders the substrate more paintable. Exceptions to either the waterborne or solventborne material class do exist, for example, in the pretreatment processes utilized on thermoplastic polyolefins. In these instances, the surface preparation consists of exposure to plasma, corona, or benzophenone/UV radiation to render the substrate paintable.

The surface cleaner generally acts to remove greases, oils, and drawing compounds from the substrate to prevent paint adhesion loss when coated. In the case of the plasma, corona, or benzophenone/UV radiation exposure of a substrate, the surface is oxidized to promote paint adhesion.

Most solventborne cleaners are based on either methylene chloride or trichloroethylene due to their superior solvency power for greases and oil. At times, isopropanol and naphtha are used on solvent-sensitive plastics such as polycarbonate to prevent degradation of the substrate. However, recent environmental regulations, i.e., the Clean Air Act of 1990, will severely limit or eliminate the use of such cleaners in the future.

Waterborne cleaners are either acidic or basic in nature. Today most cleaners are acidic so that residue remaining as a possible contaminant on the surface does not interfere with topcoat cure.

Waterborne surface cleaners are often applied to substrates in a three-to-nine-zone process. Each zone consists of a specific cleaning or conditioning step. Pretreatment or surface cleaning systems are often limited by space considerations and are designed functionally to adopt as near state-of-the-art as possible. Required zones or stages consist of surface cleaner followed by a water rinse and ending with a deionized water rinse. Additional stages can be added to accomplish several cleaning processes, conditioners, and water rinses. Additional rinsing stages provide more security in removal of trace contaminants, which could lead to topcoat adhesion problems.

After surface cleaning, the substrate is coated and tested to topcoat specifications. In order to be qualified as an appropriate cleaner, the topcoat should conform to all designated testing requirements.

Primer (Nonweatherable)

Electrodeposited Primer

Anodic electrodeposition was first introduced in the 1960s and was subsequently replaced by the cathodic process in the 1970s. Approximately 75% of all cars manufactured in the world are primed using this process.

Following pretreatment, metal parts are immersed in the electrocoat dip tank. The paint itself is 75 to 95% water. Upon application of an electrical potential, i.e., voltage, a paint film possessing 85 to 100% solids is deposited upon the parts.

Once deposited, the paint film acts as a resistor, increasing the resistivity as the film thickness increases. This accounts for the fact that as one area of a part is coated, uncoated, or relatively less coated, areas draw increased current, resulting in a very uniform coating regardless of the substrate shape or complexity.

The electrocoat technology, often consisting of an amino extended epoxy resin cross-linked with a blocked isocyanate, provides corrosion protection over cold-rolled steel for up to 400 to 500 h in a salt fog cabinet. Normal film builds of the dried electrocoat film range from 0.8 to 1.5 mils. The electrocoat technology is referred to as normal build, low build,

[1]Technical specialist, Plastic Trim and Products Division, Ford Motor Co., 24300 Glendale Ave., Detroit, MI 48239.

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high build, or high build and a half, depending on the film thickness achieved.

Conductive Primer

A conductive primer, as the name implies, provides an electrical charge to the surface of a plastic to render it paintable by electrostatic methods. Transfer efficiency of topcoats is thus improved.

The conductivity in the dried paint film is achieved most often through the use of a conductive carbon black pigment. The pigment-to-binder ratio of the conductive primer is adjusted to obtain a dry film conductivity of at least 140 Ransberg units (measured on a Ransberg meter), $<1000\ \Omega$, at a thickness of 0.8 to 1.2 mils.

As mentioned above, the conductive primer is utilized only on plastics since metal is capable of holding a potential. Conductive primers are utilized over both rigid and flexible plastics. Through modifications in the chemistry of the primer, flexibility requirements, i.e., over flexible plastics, can be achieved.

Nonweatherable primers, as the name implies, are not ultraviolet resistant. They must be topcoated. The primer can be of a one-component or two-component nature, depending upon the process capability. The chemistry of the one-component primers for rigid substrates is often comprised of an epoxy ester or alkyd cross-linked with a melamine, while flexible nonweatherable one-component primers consist of a polyester resin cross-linked with a melamine. Two-component primers, on the other hand, are based upon the same basic binder chemistries cross-linked with aromatic isocyanates in the nonweatherable class.

Nonconductive Primer

A nonconductive primer is not capable of holding an electrical potential and is utilized to provide a "Class A" surface. A "Class A" surface is a surface which, when topcoated, will provide the same appearance characteristics (gloss and distinctness of image) as a topcoated metal part. The nonconductive primer can be utilized over metal or plastic parts to provide filling characteristics to porous or marred surfaces.

The chemistry of a nonconductive, nonweatherable primer is often the same as that employed in the conductive primer. Film thicknesses range from 0.8 to 1.2 mils. Very often, the nonconductive primer is utilized over only rigid substrates, i.e., metal and rigid plastics. The primer can be "color keyed" to the topcoat color (i.e., red if a red topcoat is to be applied) so that aberrations in the topcoat (i.e., chips, scratches) will not be as noticeable.

Primer (Weatherable)

Primer/Surfacer

Weatherable primers are utilized to provide a UV durable finish over mostly flexible plastics. The primer is often color coordinated to the topcoat color to provide an aesthetically pleasing accent color. One could also refer to weatherable primers as monocoat topcoats.

Primers in this class are mostly flexible acrylic or polyester-based resins cross-linked with melamine (one-component) or an aliphatic isocyanate (two-component). They must meet the same flexibility requirements as topcoats at 1.2 to 1.5 mils. Flexible, weatherable, nonconductive primers are only utilized over "Class A" plastics.

Conductive Primer

Weatherable, conductive primers can be utilized over flexible or rigid substrates to provide a part which can be electrically grounded. The requirements for conductivity are much the same as those described above for nonweatherable conductive primers with conductive pigments utilized to provide resistance.

Weatherable conductive primers are often utilized in rub-strip areas, i.e., the black strip on a bumper or fascia, to provide a two-tone appearance. Accent colors are applied adjacent to the conductive primer to provide aesthetically pleasing parts.

Weatherability requirements are much the same as those described later for monocoat technology. The chemistry utilized to achieve the weatherable nature of the primer is the same as that described above for weatherable primers.

Topcoats

Interior Topcoat

An interior topcoat is utilized to provide a protective and decorative surface suitable for use on interior parts made of steel, aluminum, zinc-based die castings, plastics, pulp preform molded board, or other substrates. The topcoat often provides a particular feel, i.e., "soft leather feel," or a desired gloss, i.e., less than 6/60° gloss meter, to stop blinding reflections.

The chemistry of the interior topcoat varies depending on the curing process utilized, i.e., air-dry, low-temperature, or high-temperature cure. Acrylic and urethane technology have been the major chemistries utilized. On hard-to-coat substrates, a primer is often utilized to gain adhesion.

Weatherability and "fogging" are two important test specifications to which the topcoat must abide. "Fogging," described later, refers to the migration of plasticizers in the coated substrate. This is of particular concern on instrument panels and dashboards since embrittleness of the substrate and/or windshield contamination will occur.

Exterior Topcoats

Monocoat—A monocoat technology, as the name implies, is a final single coat which provides color, gloss, DOI (distinctness of image), and durability. It is applied to a total dry film thickness of between 1.5 and 2.5 mils depending upon color and hiding requirements. It should be satisfactory for use over specified primers, sealers, or other enamels, as in repair or two-toning operations. Paints specified under this standard can contain acrylic resin, urethane resin, alkyd resin, etc. as the main binder which is subsequently cross-linked with a melamine resin [referred to as a one-component (1K) paint] or an isocyanate resin [referred to as a two-component (2K) paint]. Necessary pigments and additives are blended and included to achieve final color match. Paints shall not contain toxic substances such as chrome, cadmium, etc. under the Toyota specification.

The chemistry of the monocoat is modified as needed to reflect its use over flexible or rigid substrates. The corresponding cure requirements are matched with the substrate

to be coated so as not to exceed the heat distortion temperature of the plastic parts.

Basecoat/Clearcoat—The specifications for a basecoat/clearcoat are much the same as those required of an exterior monocoat in that they require color match to a standard, a particular gloss and DOI, and a minimum durability. The basecoat, containing the necessary pigments and additives to match a particular color standard, is applied to a dry film thickness of 0.3 to 1.2 mils depending on color. It should be satisfactory for use over specified primers, sealers, or other enamels, as in repair or two-toning operations. Paints specified under this standard can contain acrylic resin, urethane resin, alkyd resin, etc. as the main binder which is subsequently cross-linked with a melamine resin (1K) or an isocyanate resin (2K). Paints shall not contain toxic substrates such as chrome, cadmium, etc. under the Toyota specification.

The clearcoat is applied over either a wet (not fully cured) basecoat (referred to as a wet-on-wet application) or a dry (cured) basecoat (referred to as a bake-on-bake application) to provide required gloss, DOI, and "wet look" depth to the cured finish. The clearcoat is applied to a dry film thickness of 1.8 to 2.0 mils. It can contain acrylic resin, urethane resin, alkyd resin, etc. as the main binder which is subsequently cross-linked with a melamine resin (1K) or an isocyanate resin (2K). Necessary ultraviolet absorbers and hindered amine light stabilizers are added to the clearcoat formulation to provide the required exterior durability.

As in the monocoat technology, the chemistries of the basecoat/clearcoat are modified to reflect their use over flexible or rigid substrates. Cure requirements are also designed to reflect the heat distortion temperatures of plastic substrates.

REQUIREMENTS

Material Requirements

Hiding (ASTM D 2805)

ASTM Test Method for Hiding Power of Paints by Reflectometry (D 2805) covers the determination, without reference to a material paint standard, of the hiding power of paints with Y tristimulus values greater than about 15%. It uses the Kubelka-Munk equations to calculate the hiding power from reflectance results obtained by broad-band filter reflectometry. It is utilized by General Motors for all automotive exterior topcoat materials.

Dry Hiding (Ford Laboratory Test Method BI 1-4)—A basecoat is required to provide complete visual hiding at specified film thicknesses (18 to 23 μm unless specified for special colors) over a black and gray straight-line hiding chart.

1. *Black and Gray Straight-Line Hiding Chart*

Hiding chart is 50 by 280 mm, consisting of a black stripe of 25 by 280 mm and a gray stripe 25 by 280 mm in a side-by-side configuration.

2. *CIE L*a*b* Hiding Chart Values*

Black:	L*	25.74
	a*	−0.13
	b*	−0.11
Gray:	L*	65.61
	a*	−1.55
	b*	9.84

(utilizing 10° Standard Observer and Illuminant D65).

PFUND Crytometer Hiding Power—The hiding power in Chrysler Material Standard MS-PP1-1 covering paint requirements and performance over plastics is determined with a Pfund crytometer, utilizing the 0.09-mm (0.0035-in.) wedge (unless otherwise specified). The hiding power is specified in the material standard covering the individual coating.

Odor

The material's odor is reviewed in reference to current production materials. Any significant differences must be evaluated in laboratory and production trials. Odor testing is performed at an approved laboratory.

Flammability

Although not a requirement for the supplier, a flash point of below 27°C necessitates the user to classify paint as a potential fire hazard. Plant security must assure that proper fire precautions are provided.

Smoke Characteristics—General Motors requires that a material's tendency to smoke during processing be reviewed in comparison to current production materials. Any significant differences must be evaluated in laboratory and production trials.

Ultraviolet (UV) Transmission

For exterior topcoats, General Motors and Ford require that a coating be opaque to UV transmission to the underlying primer layer or substrate at a film thickness 20% less than the minimum of the recommended film build range. The coating shall have been baked at the maximum of the acceptable cure range on its bake time and temperature process control chart. Opacity is defined as no transmission between wavelengths of 290 to 350 nm.

Solvent Emissions

All topcoat materials must meet specific plant solvent emissions restrictions at spray viscosities which yield acceptable applied appearance. Chrysler specifies that the material shall comply with all the requirements of the Clean Air Act (USC 1857, as amended) and any applicable federal, state, or local statute pertaining to the establishment and maintenance of the National Ambient Air Quality Standards as administered by the Environmental Protection Agency (EPA) or any authorized state or local governmental unit. The material shall comply with all of the requirements of the Water Pollution Control Act (PL 92-500, as amended) and shall be formulated to eliminate, as far as possible, constituents that would be classified as hazardous under the Resource Conservation and Recovery Act (40CFR 260-265, as amended). The material shall contain no benzene, chlorinated, or other toxic compounds.

Percent Solids by Weight—The weight solids of a material are determined according to ASTM Test Methods for Volatile Content of Coatings (D 2369B).

Percent Solids by Volume—The volume solids of a material is determined according to ASTM Test Method for Volume Nonvolatile Matter in Clear or Pigmented Coatings (D 2697).

Volatile Organic Compounds (VOC)—The volatile organic compounds (VOC) of a material is determined according to ASTM Practice for Volatile Organic Compound (VOC) Content of Paints and Related Coatings (D 3960).

Density—The density of a material is determined according to ASTM Test Method for Density of Paint, Varnish, Lacquer, and Related Products (D 1475).

Viscosity

1. *Newtonian Viscosity*

For Newtonian materials, the viscosity is measured according to ASTM Test Method for Viscosity by Dip-Type Viscosity Cups (D 4212) with a dip-tank viscosity cup.

2. *Non-Newtonian Viscosity*

For non-Newtonian materials, the viscosity is determined according to ASTM Test Method for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield) Viscometer (D 2196) with a rotational (Brookfield) viscometer.

3. *Viscosity Stability*

The stability of a material to settling or change in viscosity is usually conducted at package viscosity (as shipped). Tests are run after standing for 90 days at room temperature and as a function of accelerated heat aging (oven stability). The material after aging must be free of settling which cannot be dispersed by normal agitation and must not increase in viscosity by a percentage of its original viscosity.

Throwpower

The throwpower, in reference to cationic electrodeposition coatings, is the degree to which an electrodeposited film coats interior or recessed areas. Specific requirements are dependent upon voltage, resin type, and auxiliary electrode type and will vary by production plant.

pH

The pH of waterborne materials shall be determined according to ASTM Test Method for pH of Aqueous Solutions with the Glass Electrode (E 70) and for electrocoat baths according to ASTM Test Method for Measurement of Apparent pH of Electrocoat Baths (D 4584).

Resistivity/Conductivity

The resistivity of a material shall be determined according to ASTM Test Methods for Electrical Conductivity and Resistivity of Water (D 1125).

Performance Requirements

Color

The material shall match the appropriate master color standard after all the baking cycles for the particular color.

Gloss

The gloss of an interior coating is measured on a Hunter specular glossmeter at 60° and shall be specified by means of a letter suffix to the color number assigned by styling as follows:

A 92 min	F 35 ± 3
B 80 ± 4	G 20 ± 3
C 70 ± 4	H 10 ± 3
D 62 ± 3	J 6 max
E 50 ± 3	

The gloss of exterior topcoats is measured on a Hunter specular glossmeter at 20° and should be a minimum of 90 with no more than 4 units decrease in gloss after rebake.

Distinctness of Image (DOI)

The material shall be subjected to a DORIGON (distinctness of reflected image goniometer) and shall be within specified materials standard values.

Appearance

The topcoat shall be smooth and uniform, free of sags, craters, pinholes, seediness, abnormal roughness, or excessive metallic mottling. It shall have reasonable tolerance for ordinary cleaning and exhibit excellent polishing characteristics.

Film Thickness

A material's film thickness shall be determined according to ASTM Test Method for Nondestructive Measurement of Dry Film Thickness of Nonmagnetic Coatings Applied to a Ferrous Base (D 1186).

Hardness

The material shall have sufficient hardness to resist marring through normal handling.

Micro Hardness—The microhardness of materials applied over rigid substrates shall be determined on a TUKON hardness tester according to ASTM Test Methods for Indentation Hardness of Organic Coatings (D 1474A).

Taber Wear Resistance—There shall be no material removal greater than the approved reference panels when tested according to ASTM Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser (D 4060-81).

Adequacy of Cure

Upon subjection to solvent exposure by (methyl ethyl ketone or xylene) double rubs with a cloth, there shall be no transfer of the material's color nor dulling or softening of a clearcoat.

Adhesion

Initial Adhesion—The film shall adhere tightly and not flake, crack, or powder from the substrate. When scribed with a crosscut (X-scribe) or crosshatch, the coating should maintain a minimum of 99% adhesion after taping the area.

Moisture Resistance—After exposure to 100% relative humidity [ASTM Practice for Testing Water Resistance of Coatings in 100% Relative Humidity (D 2247)], the coating should maintain 99% adhesion when tested as above.

Gravelometer

The chip resistance of a coating is determined according to SAE J400 and ASTM Test Method for Chip Resistance of Coatings (D 3170). The chipping shall not exceed a predetermined ranking.

Toughness

Dime Scrape—The material shall not flake, peel, or lose adhesion upon subjection to scribing with a dime. This test shall be performed only on rigid substrates.

Knife Scrape—The material shall not flake, peel, or lose adhesion upon subjection to scraping with a knife. This test shall be performed on flexible substrates only.

Fluid Resistance

When subjected to the specified fluids by the methods and times specified in the applicable standards, the coating shall show no loss of adhesion, blistering, softening, swelling, or discoloration:

- xylene
- synthetic gasoline
- synthetic gasohol
- naphtha
- recommended cure check solvent
- tap water
- acid rain mixture

Immersion Test—The material shall show no loss of adhesion, blistering, softening, swelling, or discoloration when subjected to immersion testing in the specified fluids according to ASTM Test Method for Effect of Household Chemicals on Clear and Pigmented Organic Finishes (D 1308).

Cold Checking Resistance

The material shall withstand a minimum of 10 to 15 cycles of exposure to heat, humidity, and freezing conditions (at specified times and intervals) with no resultant cracking, crazing, or adhesion loss.

Crock Resistance

The material shall not transfer any color onto a cloth when exposed to the dry crock method set out in the SAE J861 method.

Flexibility

Coatings intended for use on flexible or semirigid substrates shall exhibit no cracking or induced substrate failure when subjected to bending over mandrels of various diameters at predetermined temperatures.

Water Resistance

The material shall not blister, dull, wrinkle, or peel when subjected to controlled condensation according to ASTM Practice for Testing the Water Resistance of Coatings Using Controlled Condensation (D 4585) method and X-scribed.

Weatherability

Test panels for Florida durability (facing 5° south from horizontal) and accelerated weathering durability are prepared in accordance with manufacturer's recommendations for film thickness and bake. The coating shall meet customer goals for useful life as measured by gloss retention and general appearance guidelines (color, adhesion, etc.).

QUV Exposure—Accelerated exposure is run according to SAE J2020 or ASTM Practice for Operating Light- and Water-Exposure Apparatus (Fluorescent UV-Condensation Type) for Exposure of Nonmetallic Minerals (G-53) methods dependent upon coating type and use (i.e., interior or exterior). Limits for exposure length are set by the manufacturer.

Weatherometer—Accelerated exposure is run with a carbon arc or a xenon arc for a specified interval dependent upon coating type and use. Limits for exposure length are set by the manufacturer.

Fadeometer—Interior coatings are run for a specified time period (usually 100 h) on a Fadeometer and shall not exhibit any discoloration, dulling, or adhesion loss.

Fixed Glass Bonding

Any coating intended for use in glass bonding areas must be qualified to the requirements for a new topcoat material intended as the bond surface. The coating is measured for its adhesive and/or cohesive strength to structural adhesives in a lap shear test.

Corrosion Resistance

There shall be no blistering or more than 3-mm rust creepage or loss of adhesion from a line scribed through to bare steel when exposed to salt spray resistance according to ASTM Test Method of Salt Spray (Fog) Testing (B 117) conditions for a specified time interval.

Permeability

For porous plastic substrates, i.e., SMC (sheet molding compound), certain manufacturers are requiring that coating materials be tested to solvent penetration resistance standards. General Motors, in particular, has developed a "fluorescent dye microscopy" test to limit the amount of solvent permeation into SMC from conductive primers.

Process Requirements

Basic property feasibility must be established as part of material qualification with each automotive manufacturer. Boundary conditions for key process control parameters must be established as to their effects on film build, appearance, and durability.

Viscosity

Viscosity versus temperature charts at various shear rates must be furnished.

Color Feasibility

A statistically designed experiment matrix must be run on a minimum of colors per standard procedure.

Transfer Efficiency

Initial comparisons will be made with current approved materials under controlled laboratory conditions to establish relative transfer efficiency.

Bake Latitude

A chart depicting acceptable, unacceptable, and marginal conditions for cure based on appearance, durability, and glass bonding (if applicable) characteristics of the coating must be furnished.

Circulation Stability

The supplier must establish that coating performance will not be degraded under typical, normal production use. Flow velocity required to maintain suspension or redisperse settled pigment must be provided prior to loading a circulation system.

Crater Resistance

Compatibility with plant-specific materials must be verified with all materials. Typical materials with which the coating must be compatible include sealers, primers, underbody deadeners, plastic substrates, competitive coatings, etc.

The sensitivity of a coating to crater from common in-plant contaminants (i.e., equipment oils, personal hand lotions, etc.) must also be established.

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Can Coatings

by Martin B. Price[1]

THE CONTAINER INDUSTRY IS A MAJOR USER of paints and coatings. The reported number of cans used in the United States per year is about 130 billion. The majority of these are coated individually, most with different coatings on each side. These coatings provide corrosion resistance, compliance with strict food safety and taste requirements, and present attractive long lasting identification characteristics to each container. The processes required for the efficient and economically acceptable manufacture of two- and three-piece cans and can ends involve complex engineering. Unique coatings characteristics are required to conform with these complex mechanical systems. A majority of the tests currently in use to ensure that all the requirements are met are discussed. A brief description of the processes for can production is included.

TABLE 1—United States production of beer and beverage cans.

	(Millions of cans)		
	1991	1990	% Change
Beer Cans			
Aluminum	38 428	38 751	−0.08
Steel	400	400	0.0
Total	38 828	39 151	−0.08
Soft Drink Cans			
Aluminum	52 955	49 235	7.6
Steel	2 855	4 090	−30.2
Total	55 810	53 325	4.7
All Beverage Cans			
Aluminum	91 383	87 986	3.9
Steel	3 255	4 490	27.5
Total	94 638	92 476	2.3

DESCRIPTION OF THE CAN INDUSTRY

The Can Coating Industry

The volume of coatings consumed by coating cans for food and beverage in the United States places the container industry among the highest users of finishes for all industries. A total of 130 billion cans were shipped in the United States in 1991, most of which were coated with decorative and protective coatings. Over 40 million gallons of coating were used with an estimated sales value of 350 million dollars. The United States is by far the largest user of cans and coatings for cans. Europe, which currently uses about 21 billion cans, is expected to double its usage during the 1990s as this form of packaging becomes more acceptable as a replacement for glass containers.

In addition to being one of the largest consumers of coatings, the metal container industry, because of the variety of coatings required to satisfy its needs, is also one of the most technically sophisticated. The type and quality of products identified with this industry are largely influenced by the unique characteristics of the can manufacturing processes. Therefore, can coating formulations are based on a variety of resins, among which are epoxy, poly(vinyl chloride), acrylic, polyester, or alkyd, oleoresinous, and phenolics. Coatings based on epoxies are often chosen for primers and for can ends, poly(vinyl chloride) for can ends, oleoresinous and phenolics for can interiors, acrylic, polyester and alkyd resins for decorative exteriors. Phenolic and amino based materials are often used as cross-linking agents. Water-based spray coatings (often epoxy-acrylic based) are commonly used as interior coatings for two-piece can bodies.

Recent modifications in coatings products used for this industry have been developed largely in response to federal and state pollution abatement requirements, to an ever increasing need for improved and accelerated production in this highly competitive field, and to the development and implementation of a variety of improved can manufacturing techniques. A significant level of product development effort continues in this field to define new and improved products.

The qualifications and required testing procedures for coatings for two-piece and three-piece containers can vary to some degree. A description of can production processes for these two major can types will be presented.

Can Production Processes

Two-Piece Can Production (Fig. 1)

About 70% of the total U.S. production or 95 billion cans used in the beer and beverage portion of the canning industry are constructed with aluminum and comprise what are commonly called two-piece cans. This can type is manufactured by press punching cups from sheets or coils of aluminum or steel. The cups are then forced through a series of rings to iron out and form a full-length can and to form the bottom dome. The product at this stage is a container with sides and a bottom representing one of the two pieces of a two-piece can. The lid, secured and sealed after filling, is the second piece.

[1]Consultant, Consolidated Research, Inc., consultant, AKZO Nobel Coatings Inc., 2205 Stannye Drive, Louisville, KY 40222.

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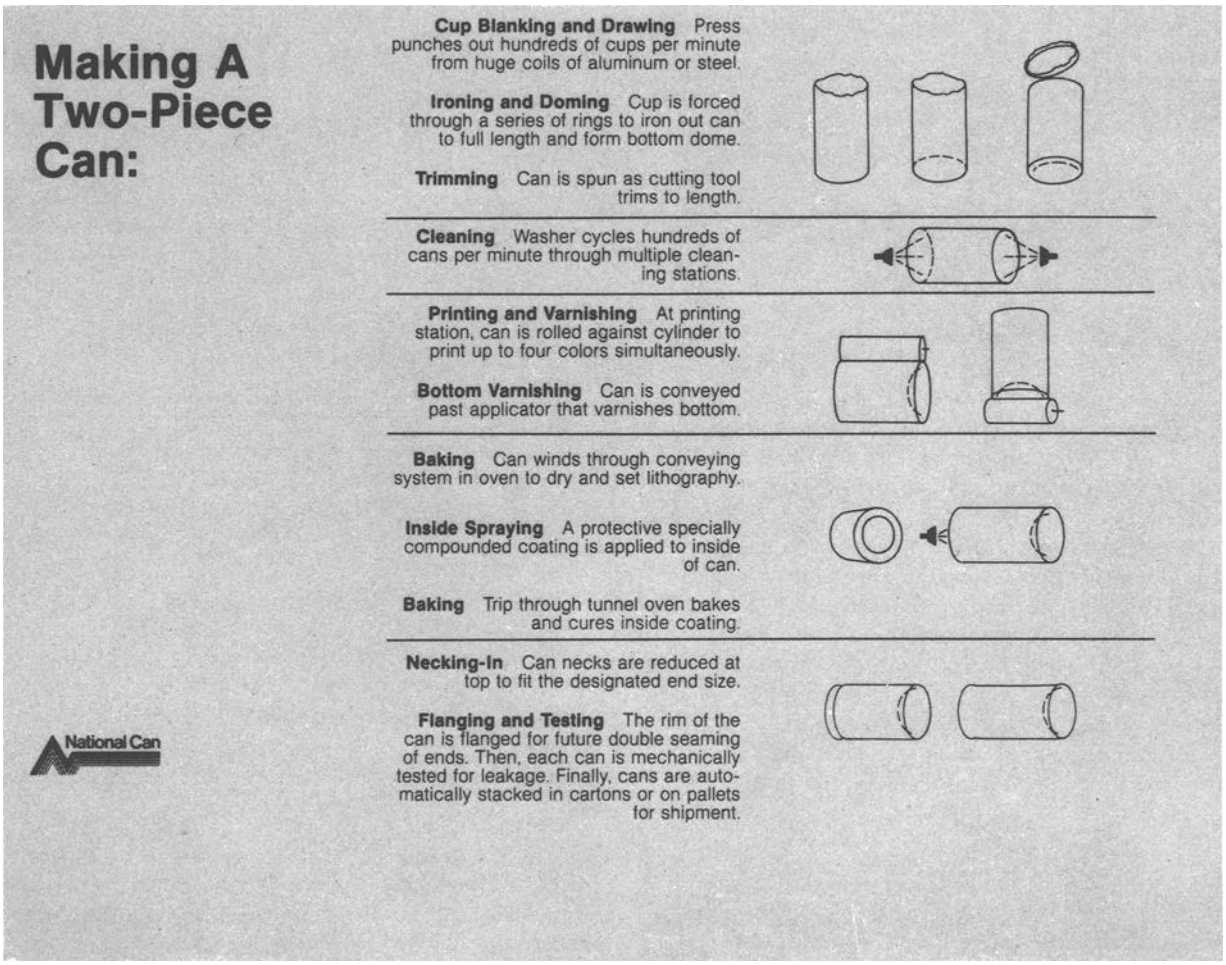

FIG. 1–Two-piece can production process.

These containers require exterior inks and coatings for decoration and identification. Increased manufacturing speed and smooth movement on the production lines requires the proper lubricity in the coating. The containers also require a high degree of abrasion resistance to maintain aesthetics and prevent can failure. Cans rubbing against each other during movement in any of many production process steps and shipping can cause scratches. These are often unacceptable for aesthetic reasons and, in extreme cases, can result in the actual rupture of the increasingly thinner stock from which cans are manufactured. It is interesting to note that cans are frequently so thin that sealing after filling with a carbonated beverage is required to give the container adequate rigidity. In addition, a level of flexibility must be inherent in the coating so that the severe crimping, which is critical to securing the lid onto the container, can be accomplished without coating failure or delamination.

Coatings are usually applied to the interior of these cans by spray techniques. Rapid application is obtained by short bursts of airless spray from a lance positioned opposite the center of the open end of horizontally held cans. This procedure is used with most food and drink containers. If the intended can content is acidic, as is the case with many soft drinks, uncoated cans can erode. Thus a coating must be applied which presents an adequate barrier to this erosion. Although beer is not strongly acidic in nature, a major concern exists regarding taste-alteration potential due to contact of the beer with metal container walls. When a protective coating is used, it cannot alter the taste of the packaged product. It is therefore necessary for beer containers, for example, to have a coating with a low level of extractables. Coatings suitable for container use (a) must be FDA compliant, (b) must pass subjective taste tests to ensure no contribution to the flavor of the product, and (c) must also meet demanding flexibility requirements. Both the interior and exterior coatings must pass most of these tests for the can production to be acceptable. For a majority of cases, after the can is packed and sealed, it is subjected to a thermal treatment to complete the processing of the contents. Many of the commercial beer products require pasteurization that is normally carried out at 150 to 180°F (65.5° to 82.2°C). Higher temperature exposures are required for processing other food products in many packaging operations. Coatings on the crimped edges of the can that may have survived the actual crimping procedure must retain adhesion, clarity, color, and abrasion resistance after these thermal treatments.

Three-Piece Can Production (Fig. 2)

In a typical manufacturing process for the three-piece can, a large metal coil is sheared into sheets. An "inside" coating is

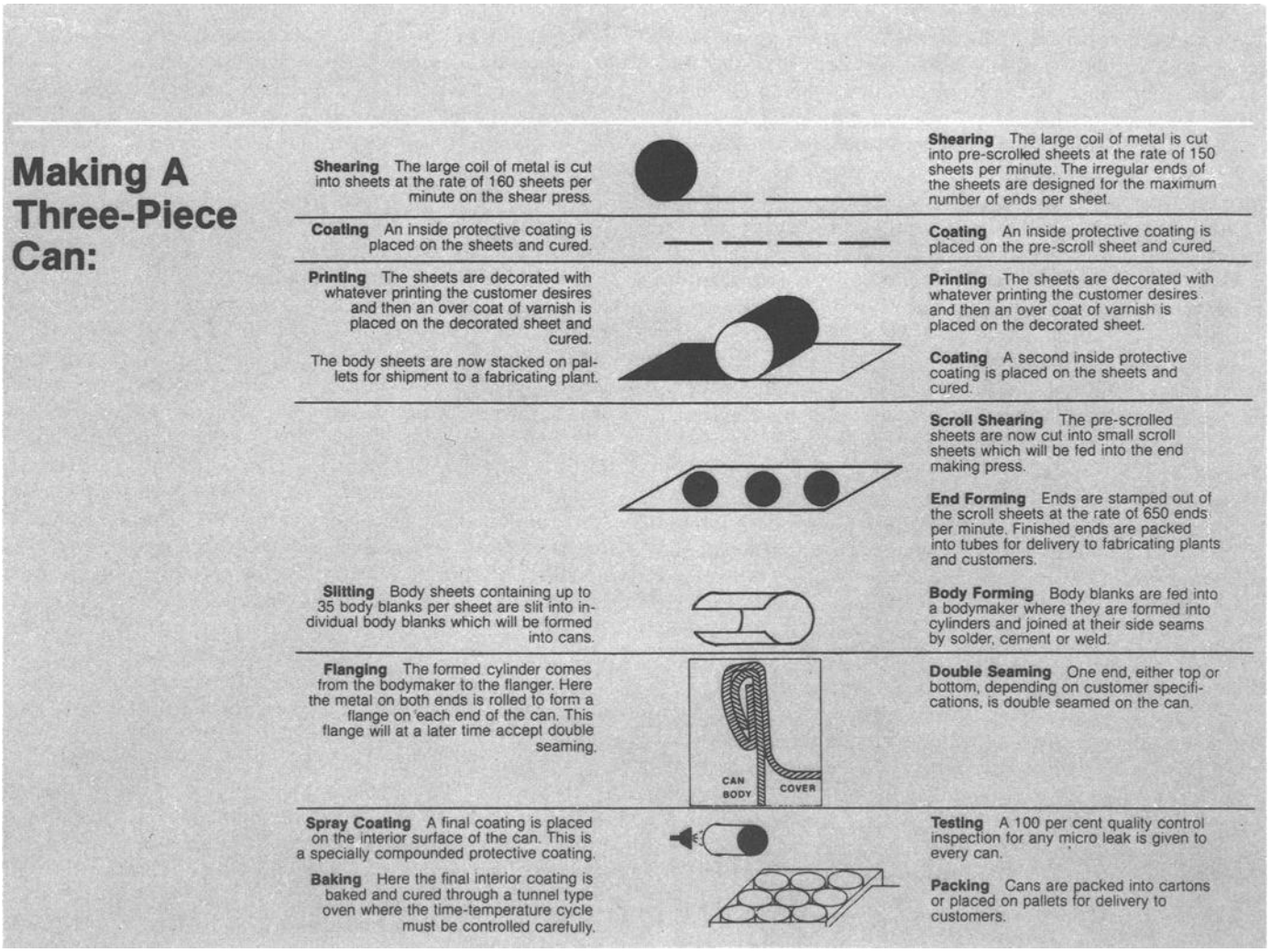

FIG. 2–Three-piece can production process.

placed on these sheets usually by roll-coater application and the coating is cured. When exterior coating is required, the "exterior" of the can is coated with the decoration defined by the customer. This decoration is often overcoated with a clear coating and the sheets are cured for a second time. On low-rust potential metal, when paper is the chosen labeling technique defined by the customer, or when ultraviolet-cured coatings are employed, this second stoving operation may not be required. (The ultraviolet cure process will be discussed later.) The coated sheets that are stacked and shipped to the fabricating plant must easily slide over one another during subsequent processing steps. The coated surface is often tested to evaluate the nonbinding characteristic of the sheets during stacking.

In the fabricating plant, the coated body sheets are slit into individual body blanks; usually about 35 body blanks are obtained from each sheet. These blanks are coiled into a cylinder shape and flanged to permit the formation of a seam that is then welded, soldered, or cemented. A coating is required to cover this seam since the initially applied coating is usually destroyed or deformed during the seaming process. A coating, either liquid or powder, is applied to this seam and cured or fused. This coating must have all the requirements of the main coating, including FDA compliance, and cause no detectable alteration to the taste of the contained product.

Preparation of Can Ends

Ends are stamped from sheets that are already coated on the side to be in contact with the packaged product. With some metals the side destined to become the exterior will also require the application of a coating to impart corrosion resistance. Can-end coatings must have the required flexibility to withstand the crimping necessary to secure the end to the top or bottom of the container. As with the two-piece can, the coating including the crimped sections must maintain integrity through the elevated temperature food processing steps.

Ultraviolet Cured Coatings

About 4 to 5% of can coating in the United States involves the use of ultraviolet curing. This process has several distinct advantages over more traditional oven-bake systems. Among these are the virtual elimination of solvents and related volatile organic compound pollutants, improved production efficiency, and low-cost plant installation. At this writing, industrial production using ultraviolet cure mainly involves external clear coatings.

The process involves the application of a photosensitive coating to the substrate, followed by a brief exposure to a selected ultraviolet wavelength at a defined intensity. The coating is hardened virtually instantaneously. In the two-piece can manufacturing process the individual cans are printed, often with ultraviolet light-curable inks, coated with a clear coating, and then exposed to ultraviolet light. The extremely fast cure permits the process to proceed rapidly to the next stage in the can production process which may be application of a water-dilutable or solvent-based interior coating. As the latter coating requires an oven bake, the ultraviolet-cured coating is oven baked as well. Only one oven pass is required.

The ultraviolet cure technique has also been used in the preparation of three-piece cans. Sheets, often printed with an ultraviolet-curable ink, are oven coated with an ultraviolet light-curable overprint coating. After radiation curing, a dry-to-touch condition required for efficient production often develops within a fraction of a second, permitting the sheet to be flipped to the reverse side. A coating which will eventually be the "inside" coating of the can is then applied and the entire sheet is cured by a standard oven process. This technique is also used for the coating of the exterior of sheets that are to be used for can ends. Again the economic advantage of only one oven pass is realized. The importance of inclusion of some measure of the speed of cure in the quality control of these ultraviolet curable coatings is obvious.

Ultraviolet coatings have been developed which meet the requirements of adhesion, flexibility, slip, gloss, abrasion resistance, and food process stability for exterior use. At this stage of their development, these coatings have not been adequately evaluated to assure compliance with FDA regulations and therefore are not available for use on interior food contact surfaces.

Testing of Can Coatings

Tests Conducted on Liquid Paint

Viscosity—As discussed in the previous section, speed of production is a critical aspect of an economically successful can production plant. The speed of application of paint required for the satisfactory coating of two-piece can bodies or of three-piece can sheets places unique requirements on the flow characteristics of the paint. To ensure complete coverage with the standard thin layer of paint, outstanding flow must be assured. The usual means for the determination of viscosity is with the use of the Brookfield Viscosimeter [ASTM Test Method for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield) Viscometer (D 2196)].

Alternate means of determining viscosity include the use of the Ford Cup or the Zahn Cup, ASTM Test Method for Viscosity of Paints, Varnishes, and Lacquers by Ford Viscosity Cup (D 1200) and ASTM Test Methods for Measurement of Wet Film Thickness of Organic Coatings (D 212), respectively. These procedures relate flow to the length of time required for a test liquid to flow through a calibrated orifice at the bottom tapered end of a cup. The Ford technique is generally considered more accurate, though less convenient than the Zahn.

Viscosity Stability—The coating can be evaluated for long-term stability by placing a sample in an oven at 120°F (48.8°C) for an extended time period. Forty days is a typical test period. The change in viscosity can be evaluated every seven days using the technique employed to rate initial viscosity. In addition, settling, agglomeration, or other changes in appearance can be noted.

Density—Density can be measured by using a Gardner™ "Weight per Gallon" cup [ASTM Test Methods for Indentation Hardness of Organic Coatings (D 1474)]. The process involves equilibrating the product to 25°C and pouring it into a cleaned cup up to the fill mark, taking care to prevent foaming. The cap is pressed onto the cup and the overflow carefully wiped from the outside of the cup. The cup is then weighed on an analytical balance and pounds/gal calculated by multiplying the number of grams of paint in the cup by 0.1.

Volatile Organic Compounds (VOC)—The determination of the VOC of a coating requires an analytical balance and an oven controllable at 110 ± 5°C [ASTM Test Methods for Volatile Content of Coatings (D 2369)]. The specimen is placed in an aluminum dish and after dilution with solvent is baked for 60 min and the percent weight loss of the sample determined. This is the percent volatile content.

The volatile organic compound content (VOC) is determined according to Federal Reference Method 24, using the weight % volatile content, the density of the liquid coating, and the weight percent water content, using the equations shown in ASTM Practice for Volatile Organic Compound (VOC) Content of Paints and Related Coatings (D 3960).

Fineness of Grind—This test is used for the determination of the fineness of dispersion of pigments in a pigmented coating. A Hegman Grind Gauge with a double-wedge steel scraper placed on a flat, nonskid surface is used (ASTM D 1260). A sample of coating is applied at the deep end of the groove of the gauge surface so it slightly overflows the total groove. The scraper is then drawn down over the entire length of the gauge with sufficient pressure to clean the sides of the gauge. A reading should be made at this point without delay. The reading consists of a visual observation made by viewing the side of the gauge perpendicularly to the drawn coating: the point where the sample shows a definite speckled pattern is read from the numbers on the side of the gauge. The quality of the dispersion is a measure of the effectiveness of the grinding operation in dispersing of pigments for pigmented coatings or of additives, such as wax, for clear samples.

Flash Point—The flash point of a coating is the minimum temperature at which vapor given off by the coating will ignite when exposed to a spark or flame. The Department of Transportation standards for shipment places a minimum flash point requirement for these coatings. A method to determine what is referred to as a closed-cup rating flash point uses a Seta Flash apparatus [ASTM Test Methods for Flash Point of Liquids by Setaflash-Closed-Cup Apparatus (D 3278)]. For an open flash point, a Tag open-cup method is often used [ASTM Test Method for Flash Point by Tag Closed Tester (D 56)]. In both methods the substance under test is heated at a controlled rate (for example, 2°/min) and a flame is passed over the surface. The flash point is defined as the temperature at which definite ignition is observed.

Cure Speed—A variety of methods have been devised for the determination of this difficult to determine and even difficult

to define characteristic of a thermoset coating. One practical definition of cure adequacy is the development of sufficient hardness in the coating that allows the can manufacturing process to advance to the next stage without marring the coating. The customer and the coating supplier frequently agree on an empirical test to satisfy cure speed requirements. A simple technique may involve the use of cotton balls. Nonadherence of fine fiber wads to a surface is often rated as adequate cure because it relates to the ability to permit the continuation of production. Frequently, a higher degree of cross-linking is required, especially for the development of resistance properties encountered by the coating at a later stage of its use. Rubbing a cured surface with a cloth moistened with a strong solvent is a method frequently employed. The determination of hardness using the pencil hardness test described later is a means of assigning a numerical rating to the relative degree of cure.

Tests Conducted on Cured Surfaces

Hardness—The hardness of a coated panel can be determined with the use of a series of pencils that have lead of various, known hardness, that is, lead with the following increasing hardness: 5B, 4B, 3B, 2B, B, HB, 2H, 3H, 4H, and 5H. For more details refer to ASTM Test Method for Film Hardness by Pencil Test—D 3363 06.01.

Film Thickness—An electric film thickness gauge can be used to determine film thickness [ASTM Test Method for Nondestructive Measurement of Dry Film Thickness of Nonmagnetic Coatings Applied to a Ferrous Base (D 1186)]. The device is calibrated with standard sheets of known film thickness placed on an uncoated surface of a similar substrate test section. After standardization, the head of the gauge is placed on the coated sample and coating thickness is reported usually in mils. The film surface is often measured at several locations on the surface of the specimen. The reported reading is the average of the several readings taken.

A StrandGauge™ is often employed in the metal decorator industry because of the ease of determining the thickness of very thin coatings characteristic of this industry. The equipment is available from the Strand Electronics Ltd., Castro Valley, California.

Film Continuity—An important characteristic of a high-quality film placed on the interior surface of a can is freedom from coating voids, meaning the absence of areas where pinholes or discontinuities exist. Can corrosion and contamination of the can contents at these voids could cause taste or color degradation. One of the accepted methods for evaluating a surface for these imperfections is an Enamel Rater Test (Fig. 3).

When using a WACO™ Enamel Rater for this test, a container to be evaluated is filled with a conductive aqueous solution and placed on a platform. Electrical contact is made on a cleaned area of the can exterior. An electrode is placed in the center of the can contents, and the amount of current flowing through the system is measured. The current flow will be impeded by the protective coating on the can interior. Flaws or breaks in the coating are areas which will permit current flow. The customers and suppliers usually agree on a maximum acceptable value.

An alternative test technique for determining film voids is the copper sulfate solution immersion test. In this test a sheet of coated metal is immersed in a solution of acidified copper sulfate for 2 to 4 min. After removal, a careful visual or magnifying glass examination of the coated metal will reveal copper-plated areas where inadequate coating protection permitted the copper to plate out onto the metal surface. The presence of flaws in the coating is an unacceptable condition for most commercial products.

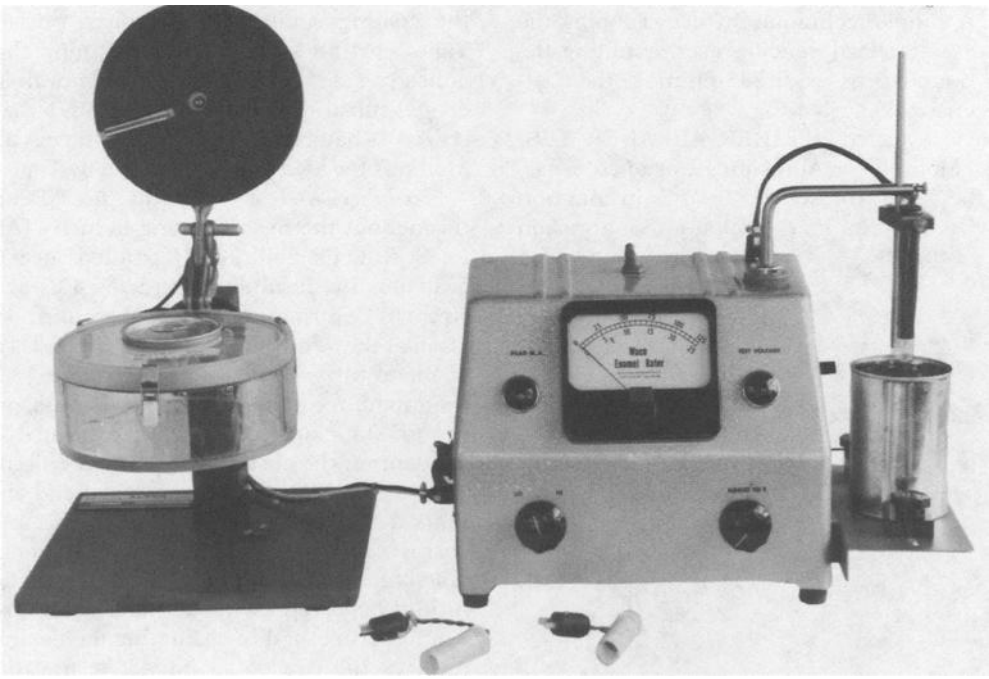

FIG. 3–WACO™ Enamel Rater test device for film voids.

Mobility/Lubricity—This important characteristic of a coating can be measured using an Altek™ Mobility/Lubricity Tester (Fig. 4).

The can or flat sample is mounted on the unit, and a test sequence is initiated by sliding a weight across the sample. The coefficient of friction is determined and is indicated directly on an electronic analog meter.

Stability to Food Processing and Pasteurization Conditions—Many foods are packed into containers in an uncooked state. Cans are sealed and the entire can is processed at an elevated temperature for the period required to complete the food processing. A characteristic test period is 1 h at 250°F (121°C) in an autoclave. Determination of the ability of a coating to withstand this treatment is often made by careful examination of a section of coated substrate which has been mandrel bent (ASTM D 1737). The section so treated is then permitted to cool and next exposed to 100% humidity, at 100°F (37.7°C) for 16 to 24 h. After cooling, visual examination of the surface for discoloration, for film rupture, and for adhesion, especially in those areas where film extension has occurred, presents a useful appraisal of the ability of the coating to withstand food processing conditions.

A less severe test is available for the pasteurization process. This is required for some foods and for some beer packaging. The temperature for this process is 150 to 180°F (65.5° to 82.2°C) for 3 h. Similar visual examination of the surface of the coated steel or aluminum substrate is conducted for discoloration or blushing, adhesion loss, or film failure.

Abrasion Testing—A critical characteristic of an acceptable exterior film is its ability to protect cans from marring and scratching the decoration and identification. As mentioned earlier in the Can Production portion of this discussion, occasionally abrasion resulting from cans rubbing against each other especially during shipment can be severe enough to actually cause rupture of the metal.

Several tests are employed to measure the coatings ability to resist abrasion. A simple technique involves rubbing the coated surface with a standard pencil eraser, counting the number of rubs or double rubs required to remove the coating and reveal the uncoated surface.

A commercial device called a TABER ABRADER TESTER™ [ASTM Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser (D 4060)] is in common use in the industry for a preliminary evaluation of abrasion resistance. In this test, coated panels are rotated under selected weighted abrasive wheels. The value is often reported as weight loss in milligrams/cycle × 1000. Another specific test requires the use of a Gavarti™ Gv Cat Test Unit (Fig. 5).

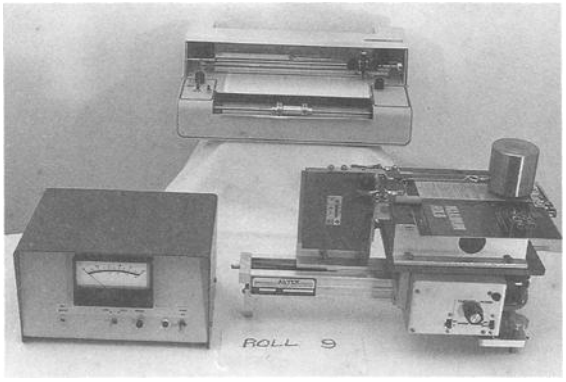

FIG. 4–Altek™ Mobility/Lubricity Tester.

This device involves the mounting of a limited number of specimens and can evaluate coated metal abrasion resistance rapidly. The device vibrates the cans or coated strips at a rate and duration which can be controlled, emulating the abrasion received during transportation. The cans are visually examined after the allotted time of exposure and rated according to individual or customer defined standards.

Pack Testing—A requirement for packaging of many food products is that no undesirable effects on the appearance of the container or to the taste or color of the contents occur when the product is stored on a shelf for three years or more. An accelerated test to evaluate this characteristic involves the actual packaging of the substance in question in a test can. The can is sealed and exposed to the food processing conditions previously described, after which the product is aged at an elevated temperature for an extended period of time. Typical conditions are 120°F (48.8°C) with a generally accepted estimate that one month exposure at this temperature relates to one year of room temperature exposure. The coating product can be periodically examined by initiating several containers at zero time and withdrawing them selectively at one-month intervals. This test is useful for new product evaluation. A three-year actual test is usually required by most customers before they will accept a new product or a significant compositional change in a coating formulation. At the end of the test period, evaluations include can appearance, food taste, and vacuum testing. The latter is accomplished by piercing the container with a device such as a hand held vacuum unit which pierces the can and seals a gauge around the puncture. This gauge determines the pressure before can opening. Chemical reaction of the food product with coating or exposed walls can result in a pressure change.

Adhesion Test—This test is similar to one used throughout the coatings industry. It involves pressing Scotch Brand Tape™ to the surface and examining the surface and the adhesive side of the tape after removal. The surface of the coated substrate is often scored with a razor in an X pattern or a cross hatch pattern before the tape is applied [ASTM Test Methods for Measuring Adhesion by Tape Test (D 3359-83)].

Flexibility—A test known as the T-Bend test is common throughout the metal coating industry [ASTM Test Method for Coating Flexibility of Prepainted Sheet (D 4145)]. The test evaluates the flexibility characteristics of a paint on a substrate by deformation of the substrate and subsequent evaluation of the adhered coating. A 0-T bend is a bend in a section of metal turned back on itself after a 180° bend. The bend examination can be visual, microscopic, or it can use Scotch Brand™ tape or copper-sulfate exposure. This is usually dependent on the customer's stated requirements.

A second 180° bend around the bend already made represents a lesser level of flexure. A coating that satisfactorily passes examination on this surface, and that has already failed the 0-T test, will be considered a 1-T flexibility coating. A third bend represents 2-T, etc.

Another method of evaluating the flexibility of the coating involves the use of an impact testing device [ASTM Test Method for Resistance of Organic Coatings to the Effects of

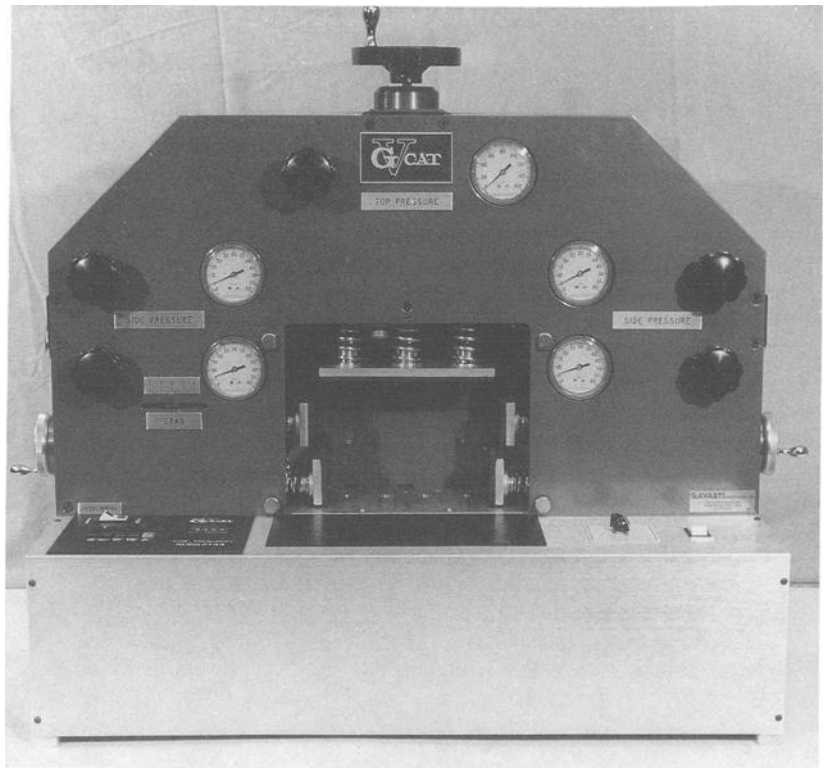

FIG. 5–Gavarti™ abrasion test unit.

Rapid Deformation (Impact) (D 2794)]. In this test flexibility is evaluated by dropping a large bullet-shaped weight from a measured height down a cylindrical guide tube onto the uncoated surface of a test sheet. The test is referred to as a reverse impact test. Microscopic examination of the impacted area is employed for evidence of cracking in the coating. The coating can be tested to the point of metal failure, a factor which depends on the thickness and strength of the substrate used.

A test more specific to the can industry involves use of the Erichsen Lacquer Testing Instrument. With this device a cup is actually formed from a section of coated metal and the corners of the formed cup are examined for signs of inadequate flexibility (T. J. Bell, Inc., 1340 Home Ave, Akron, Ohio or A. M. Erichsen, GMBH 587 Hemer, Sundwig, Germany).

Extraction Testing—Concentrations levels of coating components capable of being extracted by the container contents must be below a defined limit. The Food and Drug Administration has established a series of limits and has defined certain liquids to be used for testing based on the planned contents of the container. They are described in detail in the Code of Federal Regulations, No. 21, Section 175.300. An extraction technique is also described in detail in this government publication.

Gloss Measurement—The specular gloss of a coated sample is measured using a 60° gloss meter [ASTM Test Method for Specular Gloss (D 523)]. The meter should be equilibrated and calibrated against standard panels. The meter is placed over the panel to be tested, several readings are taken at different spots on the panel, and an average of these readings is recorded. Care must be taken to control film thickness as deviations in gloss level will be observed at varying thicknesses.

Color Measurement—The customer will assign an acceptable level of deviation of the final color of the sheets or the cans based on a defined standard. Spectrophotometric analyses using L A B ranges are reported [ASTM Test Method for Calculation of Color Differences from Instrumentally Measured Color Coordinates (D 2244)].

Blocking Resistance—Frequently, sheets of coated product are stacked and stored before being carried to the next station for processing. Such storage can often occur after an oven operation, which means that the sheets are stacked at an elevated temperature. As sheets are fed to a pile, the pressure imposed on the lower members of the stack can become considerable, and the sheets must resist adhering to each other. Efficient and rapid movement of these sheets individually for subsequent processing is essential to achieve an economical container production rate. Simple tests to evaluate the ability of coatings to resist this sticking phenomenon are commonly developed that are acceptable to both the customer and the supplier.

In one such test a series of coated sheets or panels are stacked face to back. Pressure, usually supplied via a properly placed weighted block of metal, is imposed on the top sheet or panel of the stack. The stack which can be stored at controlled temperature for defined periods of time is examined after cooling for ease of separation. The weighted block of metal is often of such a physical dimension that the resistance to sticking of the coated panels can be determined conveniently (usually reported in pounds/square inch).

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Masonry

by Frances Gale[1] and Thomas Sliva[2]

AS WITH MOST OTHER MATERIALS, masonry substrates are painted for one or both of two basic reasons: to change appearance or to improve performance in the relevant service environment. Imparting or changing color and increasing surface brightness are two important parts of the decorative function. In some cases coatings are applied to improve the appearance of the masonry substrate by masking defects or repair work. Although, in general, masonry materials do not need protection, per se, coatings can reduce attack in highly acidic atmospheres or salt water immersions. In most cases coatings help the masonry to protect the interior of the structure from penetration of moisture.

Masonry substrates to which paints are applied include stone, brick, tile, and concrete and other cement-based materials. As with other substrates, the ideal coating for masonry should be economical but must also resist soiling, retain appearance, and be easy to maintain. A coating should function effectively for a time appropriate to where it is used. Thus an exterior masonry coating should be able to withstand weathering without losing adhesion to the underlying surface.

This chapter discusses characteristics of masonry substrates that should be considered when selecting paints for application to those surfaces. Information is also provided about laboratory and field tests that are appropriate for evaluating the performance of paints.

PROPERTIES OF MASONRY SUBSTRATES

Definitions

Materials referred to as unit masonry include natural stone, brick, tile, and concrete block. Unit masonry is used in conjunction with mortar or caulk. Standard terms relating to natural building stones are defined in ASTM Definitions of Terms Relating to Natural Building Stones (C 119). Definitions for terms relating to structural clay products are contained in ASTM Definitions of Terms Relating to Structural Clay Products (C 43). In addition to unit masonry, paints are also applied to monolithic concrete. Standard terminology relating to concrete and concrete aggregates is provided in ASTM Definitions of Terms Relating to Concrete and Concrete Aggregates (C 125). ASTM Specification for Mortar for Unit Masonry (C 270) includes information about compositions and properties of different types of mortar and their uses for new construction and tuck pointing or replacement of deteriorated mortar.

Porosity

A physical property that all masonry substrates share is porosity. Their interior structures are systems of fine, interconnected pores. With some materials the pores are extremely small. However, because of this inherent porosity, all masonry is somewhat permeable to water. Hence, moisture can enter them in several ways including through poorly designed or faulty flashing, vapor barriers, etc. The presence of excessive amounts of moisture can adversely affect paint adhesion and thus performance.

Absorption Testing

The sorption of water by a masonry material is an important factor affecting the performance of the coating as well as the substrates. This is because moisture is a necessary condition for most processes of deterioration. Water absorption by masonry substrates can be determined by laboratory testing. ASTM Method of Sampling and Testing Brick and Structural Clay Tile (C 67) contains methods for testing brick and structural clay tile to determine physical properties such as absorption and saturation coefficient. Absorption is measured by submersing a representative whole tile or half brick in water for a 5-h or 24-h period. Percent absorption is determined by comparing the difference between the saturated and dry weights to the dry weight.

The test procedure for absorption by concrete masonry units described in ASTM Standard Methods of Sampling and Testing Concrete Masonry Units (C 140) is similar to that described in ASTM C 67. Three full-size units are used for testing absorption. ASTM Test Methods for Absorption and Bulk Specific Gravity of Natural Building Stone (C 97) provides a standard test method for this type of stone. The test procedure is also similar to that described in ASTM C 67 except the immersion period is 48 h. ASTM Test Method for Specific Gravity, Absorption, and Voids in Hardened Concrete (C 642) contains test methods for measuring absorption and voids in cured concrete. Absorption is calculated after a 48-h immersion and after immersion in boiling water. A method for determining the volume of permeable pore space (voids) is also provided.

[1]Training coordinator, National Center for Preservation Technology and Training, National Park Service, NSU Box 5682, Natchitoches, LA 71497.

[2]Assistant technical director, DL Laboratories, 116 E. 16th St., New York, NY 10003.

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Efflorescence

When water-soluble salts are present within the masonry substrate, efflorescence can be an unwanted result. Efflorescence is defined as a crystalline deposit of water soluble salts on the surface of the masonry material. If migration under a painted surface occurs under a painted surface, crystallization of the dissolved salts at the coating masonry interface can push the coating off the substrate. Even if the solution passes through the coating and the salts deposit on the surface, they are unsightly, and recurring efflorescence can be a symptom of deterioration taking place with the substrate. If the salts are deposited below the interface (cryptoflorescence), crystallization pressures within the masonry can lead to eventual disintegration of the masonry material.

The source of soluble salts that results in efflorescence or cryptoflorescence can be the masonry unit itself or components of the mortar. Secondary sources include contaminated groundwater and residues of chemicals used in cleaning masonry walls. A test for efflorescence of individual masonry units is contained in ASTM C 67. Full-size bricks are partially immersed in distilled water for seven days. After oven drying for 24 h, the specimens are inspected for efflorescence.

A test for assessing resistance to efflorescence is described in NBS Technical Note 883 Waterproofing Materials for Masonry. For this test one side of a brick specimen is left uncoated. The brick is placed with the uncoated surface face down in a sodium sulfate solution for seven days. After drying, the coated surfaces are inspected for efflorescence.

Surface pH

The pH of masonry substrates is variable, normally depending on the chemical composition of the material. Some materials such as brick, tile, and many natural stones have a neutral or slightly acidic pH. Others, including cement-containing materials such as concrete and calcareous stones (e.g., limestone and marble) are naturally alkaline. Mortar used with neutral or acidic masonry units can sometimes impart alkalinity to the wall surface. If the pH of the substrate is high, paints that are sensitive to alkalies should be avoided as the alkalinity saponifies them.

Surface alkalinity is not the only cause of coating failure. Subsequent migration to the surface of construction water, condensed interior water vapor through barrier defects, and capillary water from contact with the earth ("rising damp") can all result in the presence of alkalies and soluble salts.

A method for measuring surface pH is described in the ASTM Test Standard Method for pH of Chemically Cleaned or Etched Concrete Surfaces (D 4262). Although ASTM D 4262 is intended for determining whether residual chemicals have been removed following chemical cleaning or etching, the procedure for measuring surface pH of the concrete surface is described. A strip of pH test paper is placed on the wet concrete surface and compared with the color chart to determine pH.

Surface Finish

Masonry materials display a wide range of surface finishes. Adhesion of coatings to glazed tile and brick, polished stone, and highly troweled concrete is problematic because the very smooth surfaces do not develop a mechanical key. Very porous surfaces such as concrete block and natural stone such as travertine present a different sort of problem. Thin paint films do not easily cover their rough or irregular surfaces so that high-build coatings are generally used. Primers or fillers are sometimes required.

COATINGS

Both types of water-borne and organic solvent-borne coatings have been applied to masonry substrates. A brief discussion and examples of each type are provided below. Methods for determining physical and chemical properties of paints for masonry substrates appear elsewhere in this manual and in U.S. Federal Test Method Standard No. 141C. The titles of federal specifications that specifically refer to application on masonry substrates are listed in this chapter.

Water-Reducible Coatings

Water-borne or -reducible coatings are or form dispersions of the pigment, extender, binder, and additive components in water. A distinctive feature of latex coatings is that the binder is also dispersed. Consequently, most of the resulting films are porous or less compact than corresponding solvent-borne coatings and so are more permeable to water vapor. This characteristic is important as most masonry substrates contain moisture at the time the paint is applied. Water vapor permeability is also a factor subsequent to application as it is virtually impossible to completely prevent access of water to masonry walls. Transport of this water to the exterior surface, caused by thermal gradients in the winter, or to below-grade interior surfaces, caused by hydrostatic pressure, forces impermeable coatings off the surface.

Of the water-reducible coatings, portland cement powder paints have the longest service record. Cement paints form hard, flat, porous films that readily permit passage of water vapor. Cement paints help to seal and fill porous masonry surfaces. In addition to portland cement, they can contain specific additives for controlling application, setting time, water repellency, and color. Federal Specification A-A-1555 Water Paint, Powder covers cementitious type paints for protection, decoration, and waterproofing of interior and exterior masonry, concrete, and plaster surfaces. The corresponding Canadian specification was withdrawn when interior latex paints were developed. Although once widely used, cement paints have been largely replaced by latex paints.

Other federal specifications for water-reducible paints for masonry materials are TT-P-19D Paint, Latex (Acrylic Emulsion, Exterior Masonry), and TT-P-55B Paint, Polyvinyl Acetate Emulsion (for Exterior Masonry Surfaces), and TT-P-96D Paint Latex Base for Exterior Surfaces.

Block fillers are sometimes required to fill voids or holes in masonry substrates. TT-F-1098D is a federal specification for

ready-mixed styrene butadiene copolymer resin filler for cinder and concrete block and stucco.

Solvent-Borne Coatings

These materials consist of pigments dispersed in solutions of resins and additives in organic solvents. Unless overpigmented, they form smooth, continuous films that are effective moisture barriers where water intrusion must be prevented. Solvent-borne paints must be applied to dry surfaces as excessive moisture may interfere with development of adhesion and, with some coatings, cause blushing. They are, however, more tolerant than water-borne coatings to application at temperatures near the freezing point of water.

Solvent-reducible coatings are of both the thermosetting and thermoplastic type. The former type cures by oxidative polymerization (oil-modified, air-drying alkyds, and urethanes), by chemical reaction of multi-components just prior to and/or after application (e.g., epoxies and urethanes), and by heat just after application (baking alkyd, acrylic and urethane enamel). Thermoplastic coatings form films solely by solvent evaporation and include acrylic, vinyl, rubber-derivative, and cellulose-derivative resins and are by definition (although not always so called) lacquers. Federal specifications for solvent-borne coatings are TT-P-24D Paint, Oil, Concrete and Masonry, TT-P-95C Paint, Rubber, for Swimming Pools and Other Concrete Masonry Surfaces.

APPLICATION

As with any substrate, masonry surfaces must be free of dirt, oil, grease, mildew, efflorescence, and other contaminants before being coated. It is generally thought that newly constructed masonry walls should age six months before painting, but latex finishes are frequently applied much sooner. Obviously, on older surfaces, any needed repair work should be completed prior to painting. Primers are sometimes recommended for previously painted surfaces and should always be used when specified by the coating manufacturer. TT-P-00620C is a federal specification for conditioner for heavily chalked previous coatings.

Surface Preparation

As with any surface, adequate preparation of masonry substrates is essential for obtaining good adhesion of the material to be applied. With some surfaces, a simple dusting is all that is required; with others more rigorous cleaning is advisable. ASTM Practice for Surface Cleaning Concrete Unit Masonry for Coating (D 4261) and ASTM Practice for Preparatory Surface Cleaning of Architectural Sandstone (D 5107) describe procedures for cleaning with broom, vacuum, air blast, water, detergent water, and steam. ASTM D 5107 also covers a procedure for chemical cleaning.

If optimum bond of the coating to the masonry substrate is desired, alteration of the surface profile may be necessary. For concrete that will be exposed to service conditions such as continuous or intermittent immersion, temperature cycling or mechanical loading, abrading, or acid etching the surface is recommended. ASTM Practice for Abrading Concrete (D 4259) contains information on instructions for abrading concrete. Procedures described are mechanical abrading, abrasive blast cleaning, and water blast cleaning. ASTM Practice for Acid Etching Concrete (D 4260) describes some of the normal practice for this technique. In brief, the etching solution is applied to the pre-wet concrete surface, and after bubbling begins to subside, the surface is flushed with water. In both practices, a roughened, textured surface is the desired result.

Surface pH After Cleaning

Following completion of chemical cleaning or acid etching, the pH of the masonry surface should be tested to confirm that residual chemicals have been removed. This procedure is important because chemicals not removed by water rinsing may adversely affect the performance and adhesion of paints applied to the treated surface. ASTM D 4262 contains a test method for pH of chemically cleaned or etched concrete surfaces. In this method, the pH of the water rinses is taken initially and the end of the final rinse cycle.

Moisture

As stated in the subsection entitled Solvent-Borne Coatings, moisture in the masonry substrate may be detrimental to those coatings that cannot tolerate moisture at or near the surface during application. Consideration of this factor is particularly relevant following cleaning procedures that involve water (e.g., steam cleaning and chemical cleaning). ASTM Test Method for Indicating Moisture in Concrete by the Plastic Sheet Method (D 4263) contains a test method to establish whether sufficient moisture can migrate to the surface to cause problems. In this method a plastic sheet is taped to the concrete surface and allowed to remain in place for a minimum of 16 h. Following its removal, the underside is visually inspected for the presence of moisture.

The methods of sampling and testing concrete masonry units contained in ASTM C 140 include a procedure for measuring the as-sampled moisture content. As mentioned in the sections entitled "Water-Reducible Coatings" and "Solvent-Borne Coatings" above, excessive moisture in masonry may cause coatings either not to develop initial adhesion or be subsequently forced off the surface. Annex A4 of ASTM Method for Preconstruction and Construction Evaluation of Mortars for Plain and Reinforced Unit Masonry (C 780) provides a test method for determining water content of mortar sampled at the construction site.

PERFORMANCE TESTS

Field and laboratory testing are useful for evaluating characteristics thought to be essential to good performance of coatings, hence to predict their performance on masonry substrates.

Alkali Resistance

Federal Specification A-A-1555 contains a procedure for evaluating the alkali resistance of cement powder

coated panel is soaked for 14 days in a sodium hydroxide solution with the painted side ½ in. above the surface. Federal Specification TT-P-19D for latex coatings applied to wood and masonry also contains a procedure for evaluating alkali resistance.

Water Vapor Permeability

Permeability to water vapor is an important characteristic to consider when selecting masonry coatings. The parent standard for determining water vapor permeability is ASTM Standard Test Methods for Water Vapor Transmission of Materials (E 96). Although E 96 is intended for water vapor transmission of materials such as paper, plastic, plaster products, etc., the method has been used to evaluate the permeability of paints to be applied to masonry materials. In fact, Federal Specification TT-C-555b references ASTM E 96 for determining water vapor permeability.

Procedures described in E 96 that are used for evaluating masonry coatings are the desiccant (dry-cup) method and the water (wet-cup) method. Two variations are service conditions with one side wetted and service conditions with low humidity on one side and high on the other. With the desiccant method, coated specimens are placed in test dishes filled with desiccant; with the water method, they contain water. The dish assemblies are placed in chambers where temperature and relative humidity are precisely controlled. The rate of water vapor movement through the specimens is measured as a weight gain or loss versus time.

ASTM Test Method for Water Vapor Permeability of Organic Coating Films (D 1653) contains similar test methods for measuring water vapor permeability. The original version (1959), specifically for the coatings industry, attempted to cover the entire relative humidity range in one step. It was revised in 1985 to include the wet and dry cup methods from E 96. D 1653 still, however, maintains two conditions with large relative humidity ranges—the dry cup exposed to 90% relative humidity at 100°F (38°C) and the wet cup to near 50% relative humidity at 73°F (23°C). To ensure precise results, specimens must be smooth, continuous films of uniform thickness.

Field Testing

Some performance tests rely on exposing coated masonry test specimens to actual conditions in the field. ASTM Practice for Atmospheric Environmental Exposure Testing of Nonmetallic Materials (G 7) covers procedures for exposing nonmetallic materials to natural weather. Practice G 7 is intended to facilitate collection of uniform results of exposure testing by indicating the variables that should be considered and specified. Factors determining degradation due to weathering include climate, time of year, presence of industrial atmosphere, etc. The specifics of weathering, however, can be accelerated by changing the angle of exposure. ASTM Practice for Conducting Accelerated Outdoor Exposure Tests of Coatings (D 4141) includes methods for speeding up natural weathering. The greatest increase occurs when mirrors that concentrate solar radiation on the specimens also follow the sun.

Artificial Weathering Tests

Coated masonry specimens can also be exposed to simulated weathering conditions in the laboratory. It should be recognized, however, that the more accelerated the test conditions the less reliable the results.

Federal Specification A-A-1555 contains a test procedure for artificially weathering specimens. Concrete panels painted with cementitious paint are evaluated for checking, cracking, and loss of adhesion after 500 h of artificial weathering.

Although there are no ASTM methods for artificially weathering coated masonry specimens, three standard practices describe operating conditions for this testing. These are ASTM Standard Practice for Operating Light- and Water-Exposure Apparatus (Carbon Arc Type) for Testing Paint and Related Coatings and Materials (D 822), Recommended Practice for Operating Light- and Water-Exposure Apparatus (Unfiltered Open-Flame Carbon-Arc Type) for Testing Paint, Varnish, Lacquer, and Related Products Using the Dew Cycle (D 3361), and Standard Practice for Conducting Tests on Paint and Related Coatings and Materials Using a Fluorescent UV-Condensation Light- and Water-Exposure Apparatus (D 4587). Equipment used in these practices simulates deterioration caused by sunlight and water as rain or dew. Because the natural environment varies with respect to time, geography, and topography, it may be expected that the effects of natural exposure will vary accordingly.

Resistance to Wind Driven Rain

ASTM Test Method for Water Permeance of Masonry (E 514) contains a procedure for measuring water penetration and leakage through masonry to evaluate resistance to the effects of wind-driven rain. Representative materials and workmanship are used to construct test walls that are exposed to water at a rate of 138 L per square meter (3.4 gal per square foot) per hour for at least a 4-h period.

Federal Specification A-A-1555 contains a test procedure for wind-driven rain resistance of patio blocks painted with cementitious paint. Test panels are placed in a transparent plastic testing box and sprayed with 60 to 70 gal (228 to 266 L) of water per hour. Specimens are inspected at the end of 8 h for the presence of water.

Other Tests

Federal Specification TT-C-555B Coating, Textured for Exterior and Exterior Masonry Surfaces contains several procedures for testing paints to be applied to masonry substrates, including evaluating color, flexibility, impact resistance, moisture resistance, accelerated weathering, resistance to wind-driven rain, and moisture vapor permeability.

Federal Specification TT-P-19D is intended to evaluate performance of paints applied to exterior wood and masonry substrates. Concrete test panels, prepared in accordance with Federal Test Method Standard No. 141, are used for some of the test procedures.

Specimens

Obviously, the use of standardized specimens of the masonry substrate is essential to obtaining reliable data in any testing protocol. ASTM Test Method of Making and Curing Concrete Test Specimens in the Laboratory (C 192) describes the practice for making and curing concrete specimens using precisely controlled materials and conditions. ASTM Test Methods of Making and Curing Concrete Test Specimens in the Field (C 31) contains procedures for making and curing specimens using concrete delivered to the job site.

ASTM Method of Making and Preparing Concrete and Masonry Panels for Testing Paint Finishes (D 1734) contains instructions for making and preparing concrete panels for testing coatings designed for portland cement concrete. Panels are molded to fit the artificial weathering apparatus described in **Artificial Weathering Tests.** The method also describes how to mold panels for use on outdoor exposure testing racks.

Method 2051 of Federal Test Method Standard No. 141, Preparation of Concrete Panels, contains the procedure and materials required to make concrete and masonry panels for testing paints. Three procedures are described for panels with different materials and surface finishes.

SELECTION

There are a number of factors to consider when selecting paint for a masonry substrate. These include the materials and type of structure to which the paint will be applied as well as the desired appearance. As with any application, it is important to determine the service conditions under which the masonry paint must perform. Awareness of these factors should enable selection of a product that will perform effectively on masonry.

REFERENCED STANDARDS

ASTM Standards

C 31 Practices for Making and Curing Concrete Test Specimens in the Field
C 43 Definitions of Terms Relating to Structural Clay Products
C 67 Method of Sampling and Testing Brick and Structural Clay Tile
C 97 Test Methods for Absorption and Bulk Specific Gravity of Natural Building Stone
C 119 Definitions of Terms Relating to Natural Building Stones
C 125 Definitions of Terms Relating to Concrete and Concrete Aggregates
C 140 Methods of Sampling and Testing Concrete Masonry Units
C 192 Method of Making and Curing Concrete Test Specimens in the Laboratory
C 270 Specification for Mortar for Unit Masonry
C 642 Test Method for Specific Gravity, Absorption, and Voids in Hardened Concrete
C 780 Method for Preconstruction and Construction Evaluation of Mortars for Plain and Reinforced Unit Masonry
D 822 Standard Practice for Operating Light- and Water-Exposure Apparatus (Carbon Arc Type) for Testing Paint and Related Coatings and Materials
D 1653 Test Method for Water Vapor Permeability of Organic Coating Films
D 1734 Method of Making and Preparing Concrete and Masonry Panels for Testing Paint Finishes
D 3361 Recommended Practice for Operating Light- and Water-Exposure Apparatus (Unfiltered Open-Flame Carbon-Arc Type) for Testing Paint, Varnish, Lacquer, and Related Products Using the Dew Cycle
D 4141 Practice for Conducting Accelerated Outdoor Exposure Tests of Coatings
D 4259 Practice for Abrading Concrete
D 4262 Test Standard Method for pH of Chemically Cleaned or Etched Concrete Surfaces
D 4263 Test Method for Indicating Moisture in Concrete by the Plastic Sheet Method
D 4587 Standard Practice for Conducting Tests on Paint and Related Coatings and Materials Using a Fluorescent UV-Condensation Light- and Water-Exposure Apparatus
D 5107 Practice for Preparatory Surface Cleaning of Architectural Sandstone
E 96 Standard Test Methods for Water Vapor Transmission of Materials
E 514 Test Method for Water Permeance of Masonry
G 7 Recommended Practice for Atmospheric Environmental Exposure Testing of Nonmetallic Materials

Federal Standards and Test Methods

Federal Test Method Standard No. 141C Paint, Varnish, Lacquer and Related Materials: Methods of Inspection, Sampling and Testing

No. 141C, Method 2051, Preparation of Concrete Panels

12.7.7.3. Federal Specifications

A-A-1555 Water Paint, Powder (Cementitious, White and Colors)

TT-C-555B, Coating, Textured (For Interior and Exterior Masonry Surfaces)

TT-F-1098D Filler, Block, Solvent Thinned, for Porous Surfaces

TT-P-19D Paint, Latex (Acrylic Emulsion, Exterior Wood and Masonry)

TT-P-24D Paint, Oil, Concrete and Masonry, Exterior, Eggshell Finish, Ready-mixed

TT-P-55B Paint, Polyvinyl Acetate Emulsion, Exterior

TT-P-95C Paint, Rubber: For Swimming Pools and Other Concrete and Masonry Surfaces

TT-P-96D Paint, Latex Base, For Exterior Surfaces

TT-P-97D Paint, Paint, Styrene Butadiene Solvent Type, White (For Exterior Masonry)

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Pipeline Coatings

by Loren B. Odell[1] and Al Siegmund[2]

AMERICA IS THE MOST INDUSTRIALIZED NATION on earth. To run this nation, huge quantities of energy are required. Sources of energy vary, ranging from nuclear power to the burning of coal. The most common source of energy used today is based on "fossil fuels," which include oil and natural gas. In many instances, great distances are covered between the source of the fuel and its consumption. The predominant method of fuel transportation is through carbon-steel pipelines.

Pipelines are not restricted by size, product carried, or construction material. This section addresses the most common type, pipelines made of carbon-steel pipe carrying natural gas or petroleum products.

Thousands of miles of pipeline crisscross the United States. The main goal is to deliver a source of energy to the end user. Most pipelines are buried and are therefore not visible. They may be located under streets, near school yards, and near peoples' homes. Most have been in service for many years and may be in need of maintenance and/or replacement.

Building a major pipeline is a costly, time-consuming project. First, an abundant source of fuel must be located and combined with an end user. State and federal permits must be obtained, rights-of-way purchased, and financing obtained. For these and other reasons, pipelines must be long-term commitments. To protect this investment and to provide safe operations, every possible means of protection must be utilized over the service life. The most economical means of protection has proven to be a combination of coatings and cathodic protection. This section focuses on the role of coatings, their design, choice, and use.

MARKET

The U.S. Department of Commerce estimates that loss of steel due to corrosion cost $50 billion a year in the United States alone. The market for pipeline corrosion coating products can be estimated in square feet coated, or dollars of product. In 1990 this estimate for coatings grew to 300 000 ft^2 (27 870 m^2) with an estimated value of $350 000 000.

There are five basic groups of coatings used for pipeline corrosion control. They are shown below in their dollar-value market breakdown:

Asphalt enamels and asphalt mastic	7%
Polyethylene, extruded and bonded	17%
Coal tar enamels	14%
Thin film powder coatings (FBE)	32%
Tape products	30%

This distribution can vary from year to year.

WHY USE COATINGS

Corrosion control of steel pipelines is a complicated process involving several different techniques. Internal corrosion control may be accomplished with the use of coatings and/or inhibitors; external corrosion may be minimized using coatings in conjunction with cathodic protection. In all phases of corrosion control, it is recognized that coatings provide an economical, effective method of control.

In many cases it is necessary and/or advisable to use a combination of coatings with other methods of protection. Careful selection of the coating material in combination with proper application can result in years of trouble-free service. Coatings provide the widest range of protective properties, ranging from excellent mechanical properties to elevated temperature resistance. On a per-square-foot basis, coatings have proven to be the most economical corrosion control system for steel pipelines. This protection is recognized by the Department of Transportation (DOT). It is a DOT requirement that all new steel pipelines involved in interstate transportation must receive external corrosion protection in the form of bonded coatings.

EXTERNAL COATINGS

Coal Tar Enamels

Coal tar enamels are especially suitable for coating steel pipe. Generally hot applied, either in the yard or in the field, they are virtually unaffected by long periods of water immersion, soil stress, punctures, or bacteria while providing a relatively high electrical resistance. These materials work best in the temperature range of 30 to 180°F (1.1 to 82°C). Enamels are degraded by ultraviolet light and therefore should be wrapped with kraft paper when exposed. Coal tar enamels are frequently reinforced with a fiberglass mat or embedded with a felt mat as a means of protection. These products provide years of service and were the first commonly used external protective coatings.

[1]FAIC, Technical Consultant, Coatings, 416 Crestwood Drive, Houston, TX 77007 (deceased 4-9-92).
[2]Coatings Technical Services Manager, ICO, Inc., 9400 Bamboo, Houston, TX 77041.

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Coal Tar Mastic

Coal tar mastic is heavily filled with clays, silica, fiber glass, etc., which yields a highly viscous material that is cold applied to thicknesses of ½ to ⅝ in. (1.27 to 1.6 cm). This product can also be field applied as a hot extrusion seamless coating. A wide range of pipe diameters can be coated for buried pipeline service.

Coal Tar Epoxides

Coal tar epoxides are two-component materials that require mixing just prior to application. Coal tar plays two important roles in this type of coating: (1) cost reduction, (2) improved water resistance. The two components are designed to air cure, providing a harder film than neat coal tar products. Excellent adhesion is provided by the epoxy component if optimum cure is achieved.

Coal Tar Urethane

As with epoxides, coal tar is used primarily as a cost reducer. In this case, the base components are polyols and polyfunctional isocyanates, which can also be two-component spray applied to yield very rapid cure speeds. This reduces out-of-service time for the pipelines.

Coal tar products have the advantages of lower cost, excellent water resistance, wide range of application ability, and long proven service lives. They can be plant applied or over-the-ditch applied. They comprise the largest group of coatings used for the repair and maintenance of existing pipelines.

Coal tar products have limitations in protection where cathodic protection is combined with coatings. Temperature service is limited to 150°F (66°C).

Fusion Bond Epoxides (FBE)

Fusion bond epoxy coatings are one of the newest technologies viable for external protection of steel pipelines. These materials are heat-activated, chemically cured coating systems. They are 100% solid products applied in the form of "powder coatings." Powder coatings are applied directly to preheated pipe, where they melt, fuse, and cure into a continuous film. To improve application efficiency, electrostatic spray equipment is usually employed. The chemistry is such that cure often occurs through the residual heat in the pipe. This yields very rapid application parameters. Characteristics of the cured coating include excellent mechanical and physical properties. These products are also highly resistant to undercreep from cathodic protection, thereby providing long-term corrosion resistance.

FBE products have one of the highest initial costs of the external coatings and require a greater degree of surface preparation than other coatings to achieve maximum protection. They are usually plant-applied materials, although internal and external girth welds may be coated and cured in the field using portable induction heating devices for cure.

Tape and Wrap Systems

Tape-coating systems are usually cold-applied materials consisting of three layers; a primer, a corrosion-resistant interlayer, followed by a wrap in the form of a tape for mechanical protection. These systems are extremely popular for repair of existing pipelines by the over-the-ditch method of application. Each of the three layers provides special properties. The primer is frequently rubber based and modified with stress corrosion cracking inhibitors to provide good adhesion. The interlayer is olefin based to resist corrosion, while the outer layer is reinforced to resist mechanical damage and provide maximum moisture resistance.

A similar system is based on petroleum waxes. This system uses a wax-based primer, frequently combined with corrosion inhibitors, followed by an external felt or tape wrap for coating protection.

Polyethylene

This system is generally an extruded film that encapsulates the pipe using a mastic, two-part epoxy, FBE, or rubber-based primer for adhesion. The polyethylene offers excellent moisture resistance and mechanical properties. Since polyethylene is an extruded product, its application to pipe is limited to plant environments.

INTERNAL PROTECTION SYSTEMS

It is generally believed that coatings are applied to the internal surfaces of pipelines to improve product flow. As flow enhancers, they can provide increased flow rates of from 5 to 15%. These coatings do, however, provide corrosion protection; and as products carried in the pipeline become more corrosive in nature, the importance of the coatings as corrosion barriers are realized. Active lines where acid gases are involved require the use of coatings as corrosion barriers. The three systems in common use today consist of two-component epoxy polyamide/amine systems that are ambient cured, fusion bond systems that are baked, and in situ systems that are field-applied, air-dried systems based on epoxy or urethane chemistry.

APPLICATION TECHNIQUES

All of the above-mentioned coatings can be plant applied. A limited few are suitable for field application, although there are several good reasons for plant application. The first and foremost is surface preparation of the steel surface to be coated. Cleaning techniques ranging from abrasive blasting to mechanical cleaning can be mechanized and automated, resulting in a controlled surface ready for acceptance of the coating system.

This is closely followed by application technique. Automation can result in a more uniform application of the chosen coating product, resulting in film thickness control and regulation of the bake cycle for heat-cured products. Coatings that require heat to achieve chemical reaction can most economically be achieved in a plant environment.

There are outstanding coating systems that are field applied. Many are used to repair existing coated lines or to coat lines that previously had not employed coating systems. The most popular technique is an over-the-ditch system that employs both cleaning and coating equipment that travels along the pipe without removing the pipe from service. New and better methods of surface preparation that use abrasive blasting and/or high-pressure water blast are used either in conjunction with mechanical cleaning or in place of it. This technique results in cleaner surfaces for coating application. Coating compositions continue to change, improving their performance and taking advantage of new polymers to improve corrosion protection.

QUALITY CONTROL

Success is related to quality control, and the application of protective coatings to pipelines is no exception. The very best coating available can be ruined by poor application or by application to a dirty surface (Tables 1, 2, 3).

A comprehensive quality program covers all phases of a pipeline project, including steel surface quality, coating quality, and proper application of the product. The job does not end there, for improper installation of a pipeline with a good coating job can result in damage that might lead to premature failure.

The enforcement of a quality program is most easily accomplished in a plant environment. Field application is dependent upon terrain and weather conditions that can hamper required processes and procedures. A quality program that includes a representative from each step of the operation with full responsibility for their portion of the process is vital. A clear set of specifications, outlined and discussed with all parties in advance of the project, will bypass many problems. Communications between all representatives will result in a higher quality job, resulting in longer service at a lower cost.

PRODUCT DESIGN/FUTURE CONCERNS

There are several sets of specifications that pipeline coatings must meet in order to gain wide acceptance. The American Petroleum Institute (API), National Association of Corrosion Engineers (NACE), and American Water Works Association (AWWA) have specifications or recommended practices that guide in the development and use of corrosion-resistant coatings. Most specifications are part of individual company purchasing contracts. These company specifications frequently contain test parameters that must be met with corresponding references to ASTM, API, NACE, and other methods.

New products are needed that take into account the ever changing environmental regulations. Coatings that provide enhanced performance at elevated temperatures are required. New systems based upon a combination of the above technologies are trying to find their place in the market. Quality programs based upon ISO/ANSI guidelines are setting the standards for future coating projects. The opportunities are never ending.

TABLE 1—Pipeline coating specifications.

Affiliation	Number	Title
API	RP 5L2	Recommended Practice for Internal Coating of Line Pipe for Non-Corrosive Gas Transmission Service
API	RP 5L7	Recommended Practice for Unprimed Internal Fusion Bonded Epoxy Coating of Line Pipe
NACE	RP T-10D	Application, Performance and Quality (Draft) Control of Plant Applied Fusion-Bonded Epoxy External Pipe Coatings
AWWA	ANSI/AWWAC210	Liquid Epoxy Systems for the Interior and Exterior of Steel Water Pipelines
AWWA	ANSI/AWWAC214	Tape Coating Systems for the Exterior of Steel Water Pipelines
AWWA	ANSI/AWWAC215	Extruded Polyolefin Coatings for the Exterior of Steel Water Pipelines
AWWA	ANSI/AWWAC203	Coal-Tar Protective Coatings and Linings for Steel Water Pipelines-Enamel and Tape-Hot-Applied
AWWA	ANSI/AWWAC217	Cold-Applied Petrolatum Tape and Petroleum Wax Tape Coatings for the Exterior of Steel Water Pipelines

TABLE 2—ASTM tests for coal tar and related products—a partial listing.

Number	Title
D 4	Bitumen Content, Test for
D 5	Penetration of Bituminous Materials
D 36	Softening Point of Bitumen (Ring and Ball)
D 71	Density of Solid Pitch and Asphalt
D 2415	Ash in Coal Tars and Pitches
D 3143	Flash Point of Cutback Asphalt with Tag Open-Cup
G 17	Penetration Resistance of Pipeline Coatings (Blunt Rod)

TABLE 3—ASTM tests for corrosion and deterioration on pipeline coatings.

Number	Title
D 1002	Adhesion to Steel (shear)
D 1044	Abrasion Resistance (Tabor)
D 2370	Tensile Strength/Elongation
D 695	Compressive Strength
D 257	Volume Resistivity
G 6	Abrasion Resistance of Pipeline Coatings
G 8	Cathodic Disbonding of Pipeline Coatings
G 9	Water Penetration Into Pipeline Coatings
G 10	Bendability of Pipeline Coatings
G 11	Effects of Outdoor Weathering on Pipeline Coatings
G 12	Nondestructive Measurement of Film Thickness of Pipeline Coatings
G 13	Impact Resistance of Pipeline Coatings (Limestone Drop)
G 14	Impact Resistance of Pipeline Coatings (Falling Weight)
G 19	Disbonding Characteristics of Pipeline Coatings by Direct Soil Burial
G 20	Chemical Resistance of Pipeline Coatings

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Sealants

by Saul Spindel[1]

SEALANTS ARE PRODUCTS INSTALLED into an opening to prevent the intrusion of air, water, dust, heat, cold, and other materials such as gases, e.g., radon. The sealant is installed into the opening by gun or knife. It is then expected to function even though the space it occupies is stressed because of movement, thereby placing significant strain upon the adhesive forces that bond the sealant to the substrate to which it is attached. The sealant is also expected to function regardless of whether it is applied to a horizontal opening or a vertical one or whether it is applied to a building facade subject to rapid expansion and contraction or to a plaza or deck where it is subject to puncture by spiked heels.

The opening, or gap, into which a sealant is installed is usually called a joint. The sides of the joint may be made of similar or dissimilar materials, generally varying in width from 0.250 to 2.00 in. (0.64 to 5.08 cm) with the depth of the joint usually about one half the width. When required, preformed joint fillers made of materials such as open or closed cell rubber or polyurethane foam are installed to control the joint depth. Primers are sometimes used to improve adhesion.

The typical building materials that sealants are used with are glass, steel, concrete, mortar, granite, marble, aluminum, or wood. When the sealant is installed into the joint, the surfaces the sealant contacts must be clean, dry, sound, and free of contaminants or loose particles to provide an opportunity for the sealant to perform as intended.

Caulk or sealant compounds are based on oils, latex polymers, butyl, acrylic and blocked styrene solvent-release polymers, and polysulfide, polyurethane, and silicone elastomers. The oil-based products exhibit relatively little movement capability, generally 5% or less, and thus they are traditionally installed in relatively static joints. Acrylic latex polymers can be formulated to possess significant movement, as much as ±25%, whereas the solvent-release butyl, acrylic, and blocked styrene sealants can move about ±10%. The elastomerics exhibit significant movement, with silicones moving as much as 150% (+100%, −50%).

POLYMERS USED IN SEALANTS

Oil-Based Caulks

Oil-based caulks are generally composed of drying oils, mineral fillers, thixotropes, and driers. The oil oxidizes and thereby dries slowly, though the caulk usually sets up to become paintable within a 24 to 48-h period. Oil-based caulking compounds are easy to apply, easy to tool, and are available in a range of qualities. Generally, oil-based caulks exhibit movement of about 5%. Oil-based caulking compounds are used primarily by do-it-yourselfers.

Butyl Sealants

Butyl sealants are based on polyisobutylene or polybutene, fillers such as talc and/or calcium carbonate and additives such as adhesion promoters, antioxidants, and thixotropes. Butyl sealants dry by solvent release.

Butyl sealants can be formulated to move at about ±7½ to ±12½%. They are widely used in mobile home applications. In addition, another class of butyl sealants which are prepared without volatile solvents are extensively used as the primary seal in dual-sealed insulated glass because of their very low moisture vapor permeation properties.

Acrylic Solvent Release Sealants

These sealants are similar to butyl sealants; however, they are based on polymethylacrylate polymers (or polyethyl or polybutyl polymers), resulting in medium-high molecular weight products that, when formulated with colorants, thixotropes, and additives, are used as sealants.

Acrylic solvent-release sealants exhibit movement similar to butyl sealants, namely up to ±12½%. Acrylic solvent-release sealants are versatile in that they adhere to a wide variety of surfaces and, in addition, exhibit excellent resistance to sunlight. Two prime disadvantages of acrylic solvent-release sealants are: (1) they often require heating in the cartridge when applied at cool temperatures, and (2) they can emit acrylic monomer, which is somewhat odiferous and may be toxic in enclosed areas.

Block Copolymer Sealant

Elastomeric block copolymer sealants, usually based on either styrene, styrene-butadiene, or isoprene, are another class of solvent-release sealants. These polymers exhibit excellent resistance to ultraviolet light, are effective as clear sealants, generally adhere to a wide variety of substrates, and are readily paintable. The sealants can be formulated to move about ±12½%.

[1]President, D/L Laboratories, 116 East 16 Street, New York, NY 10003.

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Polyurethane Sealants

Polyurethane sealants are available as single or multi-component products. The one-component sealant is derived from an in situ reaction of an isocyanate with a hydroxyl component. These components cure by the reaction of the isocyanate (NCO) with atmospheric moisture, forming a polyurea. The sealants contain fillers, thixotropes, additives, and adhesion promoters.

Two-component polyurethane sealants are usually based on an isocyanate-terminated polyether reacted with a hydroxyl-terminated polymer. As with other sealants, two-component polyurethane sealants are combined with fillers, adhesion promoters, and other additives and stabilizers.

Polyurethane sealants exhibit good movement capabilities, easily exhibiting ±25% movement. They generally adhere well to a variety of surfaces and are widely used in commercial applications, especially where abrasion resistance, i.e., traffic applications, is a prerequisite.

Polysulfide Sealants

Polysulfide sealants are sold as both one-component and two-component materials. Two-component sealants are formulated with polysulfide polymers, hiding and color pigments, clays, and mineral thixotropes. The second, or reactive component, consists of a curing agent (e.g., lead peroxide), adhesion promoters, fillers, and stabilizers. Both components are mixed just prior to use.

The one-component polysulfide sealants are formulated with ingredients similar to the two-component material except that the cure chemistry is different. One-component polysulfides cure by reaction with atmospheric oxygen and moisture and are generally relatively slow to attain full cure.

Polysulfide sealants can be formulated to move at ±25% and are used on a wide variety of surfaces. Polysulfides are used widely in insulated glass applications.

Silicone Sealants

Silicone sealants are primarily used as one-component products usually referred to as RTV (room temperature vulcanizing) materials. They are polysiloxane prepolymers which react with atmospheric moisture and ultimately cure to form an elastomer. Silicone sealants are cured generally by one of three mechanisms, namely:

1. *Acetoxy cure*—A reaction between methyltriacetoxy silane with polydimethylsiloxane to form an acetoxy-terminated polymer "intermediate." This material is then reacted with atmospheric moisture in order to cure. Acetic acid is liberated during cure, and its odor can readily be noted.
2. *Neutral cure*—These sealants are the result of a reaction between polydimethylsiloxane with methyltrimethoxysilane to form the "intermediate." This "intermediate" then reacts with atmospheric moisture in order to cure. Alcohol is generally liberated during the cure process.
3. *Amine cure*—In this cure mechanism, methyltricyclohexylaminosilane is reacted with the polydimethylsiloxane to form an "intermediate" which cures when reacted with atmospheric moisture. Cyclohexylamine, a heavy musty-odored material, is released during cure.

Silicone sealants can be formulated to move as much as 150% and are used in many applications, especially where long-term durability is required. Silicone sealants are the primary polymers used in structural glazing.

Acrylic Latex Sealants

Acrylic latex sealants are essentially formulated from relatively high molecular weight acrylic polymers prepared by emulsion polymerization in an aqueous media and include fillers, surfactants, additives, and thixotropes. Acrylic latex sealants dry by evaporation to form easily applied, highly weatherable products that exhibit good adhesion.

These acrylic sealants can be formulated to move as much as ±25%; however, they should not be applied at low temperatures and are not recommended for use in continuous damp or wet environments.

TEST PROCEDURES

The following is a brief summary of the test methods and procedures used to evaluate sealants. Where appropriate, reference is made to specific specifications and/or procedures where these tests are covered.

Extrusion Rate and Application Life

This test is performed to measure the extrudability of single and multi-component sealants. Single-component sealants are extruded through a cartridge of known volume and predetermined orifice at 50 psi air pressure. The time to empty the cartridge is recorded. Multi-component systems are mixed and allowed to stand for 3 h before being extruded in order to develop information on their application properties after mixing.

Rheological Properties (Flow and Sag)

This test is employed to determine the horizontal or vertical flow properties of the sealant under conditions of extreme variations in temperature. Stainless steel channels, open ended for testing vertical (non sag) sealants and close ended for testing horizontal (self leveling or pourable) sealants, are filled with the sealant and exposed at an elevated temperature (122°F, 50°C), and at a low temperature (40°F, 4.4°C). Sag (vertical displacement) is measured, and horizontal deformation is noted.

Hardness

This test is used to measure the indentation hardness of a cured sealant using a Shore A Durometer. If a sealant is too hard, it may be indicative of future problems that can result in a loss of resiliency, thereby resulting in either cohesive breaks or adhesive loss.

Effects of Heat Aging

Exposure to the atmosphere may cause loss of volatile components after cure, resulting in shrinkage, hardening, or

cracking, which may affect the durability of the sealant. This test can be used to predict premature failure. Sealant specimens are cured, then heat aged for 21 days at 158°F (70°C) and evaluated for volatility (weight loss), cracking, and hardness.

Tack-Free Time

This is the time required for the surface of a sealant to attain a tack-free state. This time may be indicative of the time interval required for the sealant to resist damage from light surface contact, job-site or airborne dirt pickup, or impinging rainfall.

Staining of Porous Substrates

This test method is useful to determine possible staining by the sealant on porous substrates. The sealant is applied to standard-size joint specimens made of porous materials such as white marble or granite. The specimens are compressed and clamped and then stored for 28 days at various conditions including room temperature, elevated temperature, and ultraviolet-fluorescent weathering. Upon completion of the exposures, the specimens are evaluated for changes in surface appearance and depth of any stain.

Adhesion and Cohesion Under Cyclic Movement (Durability)

The primary intent of an elastomeric sealant is to fill joints in buildings and other structures and thereby render them impervious to the elements. These joints are considered active, meaning that they will expand and contract with temperature.

This test method is designed to evaluate the ability of the sealant to withstand expansion and contraction with temperature change and not develop any loss of adhesion to the substrate or any cohesive cracks. When adhesion loss to the substrate or cohesive cracks within the sealant develop, water can penetrate, thereby resulting in damage to the structure.

Joints are prepared using two similar substrates. The sealant is extruded between the joints (substrates), cured, and then immersed in water for seven days. The specimens are then hand flexed and evaluated for adhesion loss. If no adhesion loss is noted, the specimens are compressed and subjected to elevated temperature (158°F, 70°C) for seven days to determine whether any heat set or deformation occurs. These test joints are then subjected to ten cycles of compression at elevated temperature (158°F, 70°C) and expansion at low temperature (−15°F, −26°C) to simulate joint movement during extreme temperature changes. (Buildings contract when cold, thereby opening up or expanding the joints. On the other hand, buildings expand when hot, thereby closing or compressing the joints.) On completion of this cycling, the specimens are examined for the presence of any adhesive bond loss or cohesive breaks.

Adhesion-in-Peel

This test is used to evaluate the adhesive characteristics of a sealant and its ability to maintain a bond to a substrate. The sealant is applied to the substrate, cured, and immersed in water for seven days. After the immersion period, the 180° peel strength of the sealant is measured and the amount of adhesive loss to the substrate is determined. An additional set of specimens is prepared, exposed to UV radiation to simulate sunlight, and then evaluated for the effect of the actinic radiation on the interface of the sealant-to-glass bond by once again measuring peel strength and adhesion properties of the sealant.

Effects of Accelerated Weathering

This procedure is used to evaluate the effects of exposure to ultraviolet radiation and water spray to simulate weathering on the sealant. After exposure, the sealant is evaluated for surface cracking. Specimens are then bent over a 0.5-in. (1.27-cm)-diameter rod under cold (−15°F, −26°C) temperature to evaluate low-temperature flexibility and brittleness.

The following section lists specifications and standards for sealants, including their sources.

SEALANT SPECIFICATIONS

Federal Specifications

TT-S-00227E	Sealing Compound Elastomeric Type, Multicomponent (For Caulking, Sealing, and Glazing Building and Other Structures).
TT-S-00230C	Sealing Compound Elastomeric Type, Single Component (For Caulking, Sealing and Glazing Building and Other Structures).
TT-S-01543A	Sealing Compound, Silicone Rubber Base (For Caulking, Sealing, and Glazing in Buildings and Other Structures).
TT-C-598B	Caulking Compound, Oil, and Resin Base Type (For Masonry and Other Structures).
TT-S-001657	Sealing Compound, Single Component-Butyl Rubber Based, Solvent Release Type (For Buildings and Other Types of Construction).

ASTM Standards

ASTM C 570	Specification for Oil- and Resin-Base Caulking Compound for Building Construction.
ASTM C 669	Specification for Glazing Compounds for Back Bedding and Face Glazing of Metal Sash.
ASTM C 834	Specification for Latex Sealing Compounds.
ASTM C 836	Specification for High Solids Content, Cold Liquid-Applied Elastomeric Waterproofing Membrane for Use With Separate Wearing Course.
ASTM C 920	Specification for Elastomeric Joint Sealants.
ASTM C 957	Specification for High-Solids Content, Cold Liquid-Applied Elastomeric Waterproofing Membrane with Integral Wearing Surface.
ASTM C 1085	Specification for Butyl Rubber-Based Solvent Release Sealants.
ASTM C 1184	Specification for Structural Silicone Sealants.

OTHER SEALANT STANDARDS

Insulating Glass

ASTM E 774 Standard Specification for Sealed Insulating Glass Units.

Highway/Bridges

SS-S-200E Sealing Compounds, Two Component, Elastomeric, Polymer Type, Jet Fuel Resistant, Cold Applied.

(American Association of State Highway and Transportation Officials [AASHTO])

LIST OF ASTM C-24 STANDARDS

C 510 Test Method for Staining and Color Change of Single- or Multi-Component Joint Sealants
C 570 Specification for Oil- and Resin-Base Caulking Compound for Building Construction
C 603 Test Method for Extrusion Rate and Application Life of Elastomeric Sealants
C 639 Test Method for Rheological (Flow) Properties of Elastomeric Sealants
C 661 Test Method for Indentation Hardness of Elastomeric-Type Sealants by Means of a Durometer
C 669 Specification for Glazing Compounds for Back Bedding and Face Glazing of Metal Sash
C 679 Test Method for Tack-Free Time of Elastomeric Sealants
C 681 Test Method for Volatility of Oil- and Resin-Based, Knife-Grade, Channel Glazing Compounds
C 711 Test Method for Low-Temperature Flexibility and Tenacity of One-Part, Elastomeric, Solvent-Release Type Sealants
C 712 Test Method for Bubbling of One-Part, Elastomeric Solvent-Release Type Sealants
C 713 Test Method for Slump of an Oil-Base Knife-Grade Channel Glazing Compound
C 717 Terminology of Building Seals and Sealants
C 718 Test Method for UV-Cold Box Exposure of One-part, Elastomeric, Solvent-Release Type Sealants
C 719 Test Method for Adhesion and Cohesion of Elastomeric Joint Sealants Under Cyclic Movement
C 731 Test Method for Extrudability, After Package Aging, of Latex Sealing Compounds
C 732 Test Method for Aging Effects of Artificial Weathering on Latex Sealing Compounds
C 733 Test Method for Volume Shrinkage of Latex Sealing Compounds
C 734 Test Method for Low-Temperature Flexibility of Latex Sealing Compounds After Artificial Weathering
C 736 Test Method for Extension-Recovery and Adhesion of Latex Sealing Compound
C 741 Test Method for Accelerated Aging of Wood Sash Face Glazing Compound
C 742 Test Method for Degree of Set for Wood Sash Glazing Compound
C 765 Test Method for Low-Temperature Flexibility of Preformed Tape Sealants
C 766 Test Method for Adhesion after Impact of Preformed Tape Sealants
C 771 Test Method for Weight Loss After Heat Aging of Preformed Sealant Tapes
C 772 Test Method for Oil Migration or Plasticizer Bleed-Out of Preformed Sealing Tapes
C 782 Test Method for Softness of Preformed Sealing Tapes
C 792 Test Method for Effects of Heat Aging of Weight Loss, Cracking, and Chalking of Elastomeric Sealants
C 793 Test Method for Effects of Accelerated Weathering on Elastomeric Joint Sealants
C 794 Test Method of Adhesion-in-Peel of Elastomeric Joint Sealants
C 797 Practices and Terminology for Use of Oil- and Resin-Based Putty and Glazing Compounds
C 834 Specification for Latex Sealing Compounds
C 836 Specification of High Solids Content, Cold Liquid-Applied Elastomeric Waterproofing Membrane for Use with Separate Wearing Course
C 879 Method of Testing Release Papers Used with Preformed Tape Sealants
C 898 Guide for Use of High Solids Content, Cold Liquid-Applied Elastomeric Waterproofing Membrane with Separate Wearing Course
C 906 Test Method for T-Peel Strength of Hot Applied Sealants.
C 907 Test Method for Tensile Adhesive Strength of Preformed Tape Sealants by Disk Method
C 908 Test Method for Yield Strength of Performance Tape Sealants
C 910 Test Method for Bond and Cohesion of One-Part Elastomeric Solvent Release-Type Sealants
C 919 Practice for Use of Sealants in Acoustical Applications
C 920 Specification for Elastomeric Joint Sealants
C 957 Specification for High-Solids Content, Cold Liquid-Applied Elastomeric Waterproofing Membrane With Integral Wearing Surface
C 961 Test Method for Lap Shear Strength for Hot-Applied Sealants
C 972 Test for Compression-Recovery of Preformed Sealing Tapes
C 981 Guide for Design of Built-Up Bituminous Membrane Waterproofing System for Building Decks
C 1016 Test Method for Determination of Water Absorption by Sealant Back-Up (Joint Filler) Material
C 1021 Practice for Laboratories Engaged in the Testing of Building Sealants
C 1083 Test Method for Water Absorption of Cellular Elastomeric Gaskets and Sealing Materials
C 1085 Specification for Butyl Rubber-Based Solvent Release Sealants
C 1087 Test Method for Determining Compatibility of Liquid-Applied Sealants with Accessories used in Structural Glazing Systems

C 1135 Test Method for Determining Tensile Adhesion Properties of Structural Sealants
C 1183 Test Method for Extrusion Rate of Elastomeric Sealants
C 1184 Specification for Structural Silicone Sealants
C 1193 Guide for Use of Joint Sealants
C 1216 Test Method for Adhesion and Cohesion of One-Part Elastomeric Solvent Release Sealants
C 1241 Test Method for Volume Shrinkage of Latex Sealants During Cure
C 1246 Standard Test Method for Effects of Heat Aging on Weight Loss, Cracking, and Chalking of Elastomeric Sealants after Cure
C 1247 Standard Test Method for Durability of Sealants Exposed to Continuous Immersion in Liquids
C 1248 Test Method for Staining of Porous Substrates by Joint Sealants
C 1249 Test Method for Secondary Seal for Sealed Insulating Glass Units for Structural Sealant Glazing Applications
C 1257 Test Method for Accelerated Weathering of Solvent Release Type Sealants
C 1265 Test Method for Determining Tensile Adhesion Properties of an Insulating Glass Edge Seal for Structural Glazing Applications
D 2202 Test Method for Slump of Sealants
D 2203 Test Method for Staining from Sealants
D 2249 Test Method for Predicting the Effect of Weathering on Face Glazing and Bedding Compounds on Metal Sash
D 2376 Test Method for Slump of Face Glazing and Bedding Compounds on Metal Sash
D 2377 Test Method for Tack-Free Time of Caulking Compounds and Sealants
D 2450 Test Method for Bond of Oil- and Resin-Base Caulking Compounds
D 2451 Test Method for Degree of Set for Glazing Compounds on Metal Sash
D 2452 Test Method for Extrudability of Oil and Resin-Base Caulking Compounds
D 2453 Test Method for Shrinkage and Tenacity of Oil and Resin-Base Caulking Compounds

CANADIAN STANDARDS

CAN/CGSB-19.0-M77—Metods of Testing Putty, Caulking and Sealing Compounds

CAN/CGSB-19.1-M87—Putty, Linseed Oil Type

19-GP-5M—Sealing Compound, One Component, Acrylic Base, Solvent Curing

CAN/CGSB-19.6-M87—Caulking Compound, Oil Base

CAN/CGSB-19.13-M87—Sealing Compound, One-Component, Elastomeric, Chemical Curing

19-GP-14M—Sealing Compound, One Component, Butyl-Polyisobutylene Polymer Base, Solvent Curing

CAN/CGSB-19.17-M90—One-Component Acrylic Emulsion Base Sealing Compound

CAN/CGSB-19.18-M87—Sealing Compound, One-Component, Silicone Base, Solvent Curing

CAN/CGSB-19.20-M87—Cold-Applied Sealing Compound, Aviation Fuel-Resistant

CAN/CGSB-19.21-M87—Sealing and Bedding Compound Acoustical

CAN/CGSB-19.22-M89—Mildew-Resistant Sealing Compound for Tubs and Tiles

CAN/CGSB-19.24-M90—Multicomponent Chemical-Curing Sealing Compound

CAN/CGSB-19.28-91—Glossary of Terms Related to Sealants

AAMA STANDARDS

801.1 Voluntary Specifications for Adhesive Type Sealant for Joints of Applied or Integral Fin
802.3 Voluntary Specifications for Ductile Back Bedding Compound for Use with Architectural Aluminum
803.3 Voluntary Specifications for Narrow Joint Seam Sealer for Use with Architectural Aluminum
804.1 Voluntary Specifications for Ductile Back Bedding Glazing Tapes for Use with Architectural Aluminum
805.2 Voluntary Specifications for Bonding Type Back Bedding Compound for Use with Architectural Aluminum
806.1 Voluntary Specifications for Bonding Type Back Bedding Glazing Tapes for Use with Architectural Aluminum
807.1 Voluntary Specifications for Oil Extended Cured Rubber Back Bedding Glazing Tapes for Use with Architectural Aluminum
808.3 Voluntary Specifications for Exterior Perimeter Sealing Compound for Use with Architectural Aluminum
809.2 Voluntary Specification for Non-Drying Sealants for Use with Architectural Aluminum

INTERNATIONAL STANDARDS ORGANIZATION STANDARDS

The following standards are under the jurisdiction of Subcommittee 8 on Jointing Products, Technical Committee 59-Building Construction:

ISO 6927 Building Construction-Jointing Products-Sealants-Vocabulary
ISO 7389 Building Construction-Jointing Products Determination of Elastic Recovery
ISO 8339 Building Construction-Jointing Products-Sealants Determination of Tensile Properties
ISO 8340 Building Construction-Jointing Products-Sealants Determination of Tensile Properties at Maintained Extension
ISO 8394 Building Construction-Jointing Products Determination of Extrudability of One-Component Sealants

ISO 9046 Building Construction-Sealants Determination of Adhesion/Cohesion Properties at Constant Temperatures
ISO 9047 Building Construction-Jointing Products-Sealants Determination of Adhesion/Cohesion Properties at Variable Temperatures
ISO 9048 Building Construction-Jointing Products-Sealants Determination of Extrudability of Sealants Using Standardized Apparatus

SOURCES OF SPECIFICATIONS

ASTM Specifications
American Society for Testing and Materials
1916 Race Street
Philadelphia, PA 19103
(215) 299-5400

ASSHTO Specifications
The American Association of State Highway
And Transportation Officials
444 North Capitol Street, NW, Suite 225
Washington, DC 20001
(202) 624-5800

Federal Specifications
Business Service Center
General Services Administration (Regional Offices)
7th and D Streets, SW
Washington, DC 20407

Military Specifications
Commanding Officer
U.S. Naval Supply Depot
5801 Tabor Avenue
Philadelphia, PA 19120
(215) 697-2000

ANSI Specifications
(Also International Standards Documents)
American National Standards Institute, Inc.
1430 Broadway
New York, NY 10018
(212) 354-3300

U.S. Army Corps of Engineers
Chief Specification Section
Box 60
Vicksburg, MS 39180

Canadian General Standards Board
Ottawa
Canada K1A 1G6

American Architectural Manufacturer's Association
1540 East Bundee Road
Palatine, IL 60067

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Traffic Marking Materials

by Larry R. Hacker[1]

TRAFFIC MARKINGS GO RELATIVELY UNNOTICED by most people but affect almost everyone every day. They are used not only on city streets, highways, and interstates but also at airports, parking lots, and many commercial and industrial sites. A variety of materials are used for these applications. Some have specific uses, but all must adhere to the surface on which they are applied, show resistance to abrasion and weathering, and perform adequately over their expected lifetimes.

The following discussion will focus on the different types of marking materials being used and the testing of these materials for acceptability.

TYPES OF PAVEMENT MARKING MATERIALS

There are three general-type materials used for pavement markings. These include liquid coatings, thermoplastics, and tapes. All pavement markings fall into one of these general categories. Glass beads are used with each of these pavement marking materials to improve night visibility. Reflective devices are also used in conjunction with pavement markings to improve visibility but are beyond the scope of this manual.

Liquid Coatings

Solvent-Borne Coatings

This is the standard coating in use for traffic marking for decades. These materials are usually alkyds or chlorinated rubbers that dry by the evaporation of their solvents, followed by oxidation of their binders. They are usually applied hot and under pressure with conventional spray equipment to achieve fast-drying markings. The advantages of using solvent-borne coatings are the vast body of knowledge and experience with these materials—they can be applied over a wide range of environmental conditions and have a low cost. The major disadvantages are the need for frequent applications, especially in high-traffic areas, the release of large quantities of solvent to the atmosphere during drying, and the need for solvent to clean equipment. These solvents contribute to air pollution and become hazardous waste when used to clean equipment.

Senior analytical chemist, Virginia Department of Transportation, 1401 E. Broad Street, Richmond, VA 23219.

Water-Borne Coatings

Within the last decade, water-borne traffic coatings have overcome many of their early problems with water sensitivity and dry time to become acceptable as traffic marking materials. Applied with the same equipment as solvent-borne coatings, favorable environmental conditions are more limited for water-borne than solvent-borne coatings. Low air and surface temperatures, high relative humidity, and low air movement will adversely affect the film formation of the coating. Washout from a rainstorm soon after application can also be a concern. With the reduction of solvent emission and hazardous waste, water-borne coatings are the traffic marking material of the future where solvent emission is a concern and favorable environmental conditions are obtainable during a large part of the striping season.

Polyester

This is a two-component system used mainly on portland cement concrete surfaces since proper adhesion is a concern on asphalt concrete surfaces. This coating is a durable, high-quality material that has a useful life of three years or more. It is used mostly in high-traffic areas where repeated application of traditional coatings would disrupt traffic, be costly, and be possibly unsafe. Adjusting mix ratios of resin and catalyst gives appropriate cure times. Some disadvantages include monomer emission, hazardous waste generated from solvents used in equipment clean up, and the need for special two-stream spray equipment.

Epoxy

This is also a two-component, durable, high-quality pavement marking material. Its applications and use are similar to the polyester material. A variety of cure times can be achieved through formulation adjustments. Close attention must be paid to the mix ratio of the components to obtain optimum performance and durability.

Thermoplastic

Thermoplastic pavement markings are another durable, high-quality marking material. This is a mixture of either maleic-modified glycerol resin esters or hydrocarbon resins with plasticizers, pigments, and glass beads. The formula is melted at 400°F (204.4°C) and can be extruded or sprayed on the surface to be marked. Thermoplastic may be applied to

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any clean surface but performs best when applied on asphalt concrete. Mixing is absolutely necessary during heating to prevent local burning of the material. Application thicknesses are usually in the 30 to 125-mil (0.229 to 0.318-cm) range.

Pavement Marking Tape

Pavement marking tapes can be used as a durable, long-life marking material or as a removable or temporary marking in construction areas. All tapes are composed of three layers: an adhesive layer, a backing material usually made of plastic or aluminum foil, and a pigment and glass bead layer. Application of these tapes will vary between manufacturers with primers being used for some tapes. All are rolled with a weighted roller to increase surface contact between the tape and the pavement.

Permanent Tapes

These tapes can be divided into plastic-backed and foil-backed tapes. Plastic-backed tapes are 60 to 90 mil (0.152 to 0.229 cm) thick and are used as stop bars, crosswalks, arrows, and long lines in lighted areas only. Foil-backed tapes are greater than 24 mil (0.061 cm) in thickness. They are used in unlighted areas that are free of curves, turns, or stops.

Temporary Tape

This tape is used on construction sites where the marking will eventually be paved over. Thickness of this tape are greater than 25 mil (0.064 cm).

Removable Tape

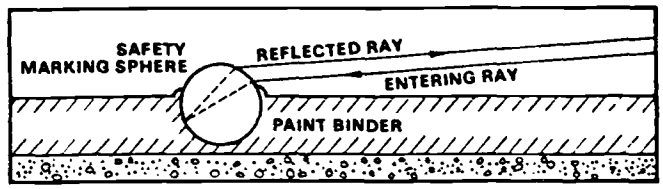
This tape is also used on construction sites but on projects that require the tape to be removed. To facilitate removal, a plastic mesh or similar material is added between the adhesive layer and the backing material of the tape. Film thicknesses are greater than 30 mil (0.076 cm).

Glass Beads

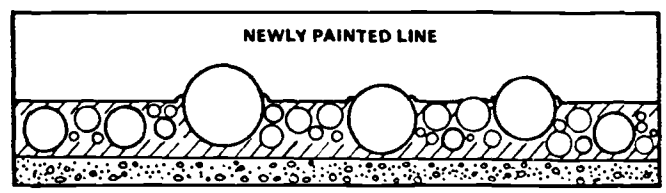
Glass beads are used with pavement markings to increase night visibility. Without the beads, most marking would be invisible at night. Figure 1 gives an excellent explanation of how glass beads improve visibility. Glass beads must be round to work. Broken beads or pieces will not refract light. Beads vary in refractive index (RI) from 1.50 to 1.90. The 1.50 RI beads are most commonly used for highways, while the 1.90 RI beads are found on airport runways. Glass beads also come in a variety of sizes with a specific size distribution usually being specified. The application of glass beads is done immediately after a pavement marking material has been applied. This is usually done by a pressurized spray nozzle so that many of the beads, about 70%, are buried in the marking material. The quantity of beads added to a line will vary with the marking material from 6 to 25-lb/gal (0.720 to 3.003 kg/L).

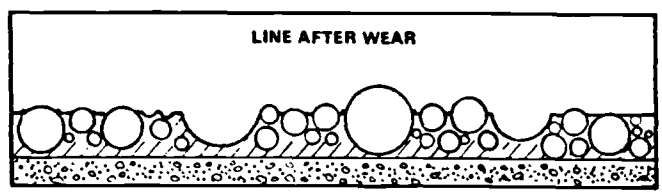
HOW DO GLASS SPHERES WORK

The reflectorization of markings which brings about the increase in night driving safety is accomplished by the use of tiny glass spheres which operate on the principle of retro-reflection. That is, they reflect light back to the source; i.e. the automobile headlight from which it came. As a result, highway lines and markings into which millions of these tiny reflective spheres have been embedded, shine brightly under headlights and are many times more visible to drivers than the same lines or markings without reflectorization.



A headlight ray entering a marking sphere is refracted to the opposite side from where it is reflected along a parallel line to the source. Non-round spheres do not reflect light but scatter it in random directions. Quality control to assure a proper number of true round spheres assures optimum retroreflection.





Safety Marking Spheres of carefully graded sizes are used to reflectorize the line. Thus, as the line wears under traffic flow and larger spheres which provide immediate reflectorization are dislodged, the smaller spheres, previously completely embedded, are uncovered and become active.

FIG. 1–How do glass spheres work? (from *Potters Safety Marking Spheres*, Potters Industries Inc.).

MATERIAL TESTING

Pavement marking materials are tested for conformance to specification in the laboratory and for performance in field evaluations.

Laboratory Testing

Liquid Coatings

Many of the tests performed on liquid coatings are standard coating tests and are referenced where applicable.

Liquid Properties

1. *Skinning*—Paints that contain binders that dry by oxidation can form skins in a partially filled container. These must be removed before use. This test can be performed in accordance with ASTM Methods of Testing Varnishes (D 154).
2. *Fineness of Dispersion*—Commonly called "fineness of grind," this test is not generally specified for traffic marking except in the case of some application equipment. The test is performed in accordance with ASTM Test Method for Fineness of Dispersion of Pigment-Vehicle Systems (D 1210).
3. *Density or Weight/Gallon*—The density is determined for unbeaded paint by using ASTM Test Method for Density of Paint, Varnish, Lacquer, and Related Products (D 1475).
4. *Consistency*—Determine the consistency using a Stormer Viscometer in accordance with ASTM Test Method for Consistency of Paints Using the Stormer Viscometer (D 562).
5. *Stability*—Traffic paints should remain stable in the container for at least six months. Stability can be checked by heating and cooling a specimen through several cycles or by storing at room temperature for a period of time. Use ASTM Test Method for Setting Properties of Traffic Paints During Accelerated Storage (D 1309) for the accelerated test and ASTM Test Method for Evaluating Degree of Setting of Paint (D 869) for an aged sample.
6. *Chemical Analysis*—Identification and quantification of traffic paint components can be made by several means. Infrared spectroscopy can be used for resin identification. Use ASTM Test Method for Infrared Identification of Vehicle Solids from Solvent-Reducible Paints (D 2621) to aid identification of solvent reducible resins. Oils and oil acids can be identified by using gas chromatography. ASTM Test Method for Fatty Acid Composition by Gas-Liquid Chromatography of Methyl Esters (D 1983), ASTM Test Method for Identification of Oils and Oil Acids in Solvent-Reducible Paints (D 2245), and ASTM Test Method for Preparation of Methyl Esters from Oils for Determination of Fatty Acid Composition by Gas Chromatography (D 2800) can be determined using either the Jones Reduction method or the aluminum reduction method found in ASTM Test Methods for Chemical Analysis of White Titanium Pigments (D 1394). Chrome yellow may be quantified using atomic absorption spectroscopy or by wet chemical methods using ASTM Test Methods for Analysis of Yellow, Orange, and Green Pigments Containing Lead Chromate and Chromium Oxide Green (D 126).
7. *Pigment Content* —ASTM Test Method for Pigment Content of Solvent-Reducible Paints (D 2371) is used for solvent reducible coatings and ASTM Test Method for Pigment Content of Water Emulsion Paints by Low-Temperature Ashing (D 3723) is used for water emulsion paints. ASTM Test Methods for Pigment Content of Paint by Low Temperature Furnace Ashing (450°C) (D 4451) is a low-temperature ashing method useful for all coatings that do not contain organic pigments.
8. *Non-Volatile Content*—Sometimes referred to as "total solids," use ASTM Test Methods for Volatile Content of Coatings (D 2369) to determine the non-volatile content of the paint.
9. *Epoxy Content*—Many epoxy traffic markings specify an epoxy content. Use ASTM Test Methods for Epoxy Content of Epoxy Resins (D 1652) for this determination.
10. *Amine Value*—An amine value is also specified on many epoxy traffic markings. Use ASTM Test Methods for Total, Primary, Secondary, and Tertiary Amine Values of Fatty Amines by Alternative Indicator Method (D 2074) for this determination.

Appearance and Physical Characteristics

1. *No-Pick-Up Time*—A quality control test that is useful in the laboratory uses a steel cylinder fitted with two replaceable O-rings that is rolled down a ramp over a test stripe as shown in Fig. 2. This is a control test and shows no correlation with field applications. The no-pick-up time can be determined using ASTM Test Method for No-Pick-Up Time of Traffic Paint (D 711).
2. *Bleeding*—This test attempts to measure the amount of material that passes from an asphalt pavement through the traffic marking material. An arbitrary scale of photographic standards are used, where 10 shows no bleeding and 2 shows considerable bleeding. Use ASTM Test Method for Laboratory Determination of Degree of Bleeding of Traffic Paint (D 969) to determine bleeding. ASTM Test Method for Evaluating Degree of Bleeding of Traffic Paint (D 868) contains the photographic standards.
3. *Hiding Power*—Hiding power is the measure of the ability of the coating to hide the substrate. Using a reflectance measuring instrument, ASTM Test Method for Hiding Power of Paints by Reflectometry (D 2805) gives the procedure for performing this determination.
4. *Color*—The color of traffic markings are usually compared to a specified standard. Color differences can be determined visually between the product and a standard. This

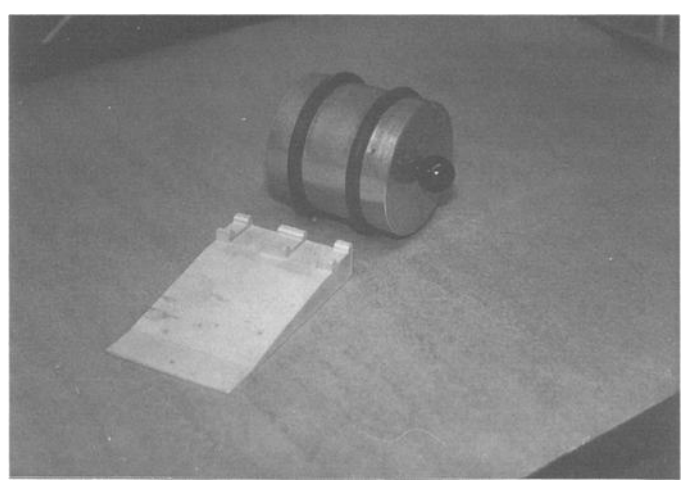
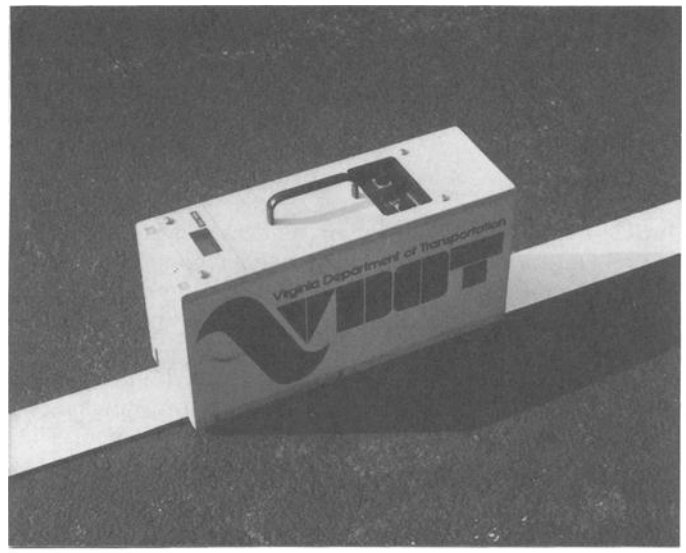


FIG. 2–ASTM D 711 equipment.

comparison is fast and acceptable although numerical values are not obtained. The advantage of using color difference instruments are that they provide numerical values that can be compared to later measurements. Visual color comparison can be made in accordance with ASTM Practice for Visual Evaluation of Color Differences of Opaque Materials (D 1729). To determine the color in terms of tristimulus values or chromaticity coordinates, use ASTM Test Method for Computing the Colors of Objects by Using the CIE Systems (E 308). Color difference measurements are instrumentally obtained by following ASTM Test Method for Calculation of Color Differences from instrumentally Measured Color Coordinates (D 2244).

5. *Reflectance and Retroreflectance*—Reflectance is the measure of light reflected from the surface of a material. To determine which of two samples appear lighter when viewed in average daylight, each sample is illuminated at a 45° angle and viewed at a 0° angle using the standard CIE source C, and the Y-tristimulus value is recorded. Determine the reflectance in accordance with ASTM Test Method E 97. Retroreflectance is a measure of light reflected close to the direction in which it came. In practice, it simulates the light reflected from a pavement marking by the vehicles' headlamps. In the laboratory, retroreflectance can be measured in accordance with ASTM Test Method for Retroreflectance of Horizontal Coatings (D 4061). Portable retroreflectometers are used to test pavement markings in field evaluations. Although there is not yet a standard procedure to use these instruments, the theory behind their use is the same as the laboratory procedure. The Mirolux 12 portable retroreflectometer which is used by several state Departments of Transportation is shown in Fig. 3. It has an internal calibration, an illumination angle of 86.5°, and an observation angle of 1.5°. After the instrument is zeroed and calibrated, it is placed over the test line and the reading is obtained. Testing has shown that there is a correlation between readings obtained with a portable retroreflectometer and those obtained in the laboratory using ASTM Test Method D 4061.
6. *Resistance to Wear*—This is a measure of a pavement markings' ability to withstand wear from traffic. The test procedure involves dropping sand on a dry test specimen until the substrate is visible. The test is usually performed on an unbeaded material that is the appropriate thickness. A variation of the test is to drop a specific volume of sand on the specimen and calculate the amount of material lost by weight. The abrasion resistance can be determined by using ASTM Test Method for Abrasion Resistance of Organic Coatings by Falling Abrasive (D 968).



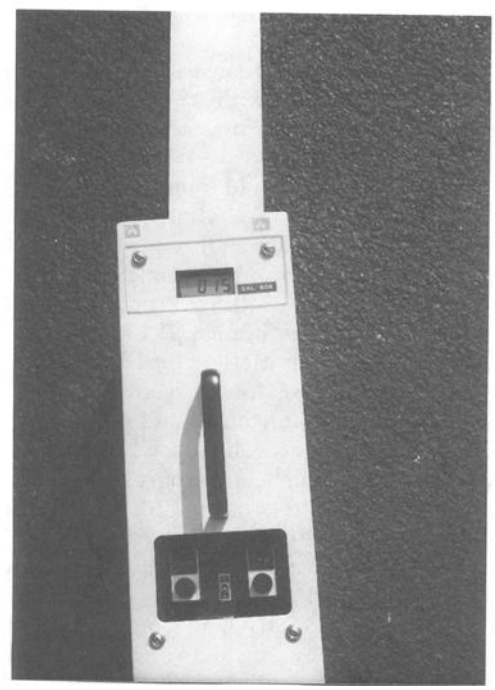


FIG. 3–Mirolux 12 portable retroreflectometer.

Thermoplastic

Thermoplastic material is supplied in a powdered form or in block form. The material is prepared for testing by melting a sample at its application temperature under constant agitation. A guideline for testing thermoplastics can be found in the American Association of State Highway and Transportation Officials (AASHTO) Standard Test Method T-250.

Gravimetric and Chemical Analysis—A melted thermoplastic patty is allowed to cool to room temperature. It is then broken into pieces and ashed in a muffle furnace at 540°C for 1 h. From this sample, the amount of binder, glass beads, titanium dioxide, or lead chromate can be determined. These can be determined in accordance with ASTM Test Methods for Chemical and Gravimetric Analysis of White and Yellow Thermoplastic Traffic Marking Containing Lead Chromate and Titanium Dioxide (D 4797).

Appearance and Physical Characteristics

1. *Reflectance*—Measuring reflectance on thermoplastic is the same as for liquid coatings except a patty is used instead of a drawdown coating. Use ASTM Test Method for Evaluation of Color for Thermoplastic Traffic Marking Materials (D 4960) to determine reflectance.
2. *Softening Point*—Thermoplastic marking material does not have a distinct melting point but will become gradually

softer as the temperature rises. The softening point is useful in predicting the tendency of the material to flow at elevated temperature. To measure the softening point, melted thermoplastic is cast into brass rings and allowed to cool. The ring of thermoplastic, which is supporting a steel ball, is placed in a liquid bath and heated at a controlled rate. The softening point is reported as the temperature at which the steel ball falls a distance of 1 in. (2.54 cm). The softening point can be determined in accordance with ASTM Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus) (D 36).

3. *Specific Gravity*—The specific gravity of the thermoplastic is determined on the premelted sample. The material is ground so it will pass through a 0.600-mm (No. 30) sieve. The thermoplastic is tested in accordance with ASTM Test Method Test Methods for Specific Gravity of Pigments (D 153) Method A to determine its specific gravity.
4. *Bond Strength*—The bond strength of thermoplastic marking material is determined instrumentally using concrete bricks and steel blocks. A melted specimen is applied to a concrete brick with a drawdown blade. Two steel cubes are placed in the hot thermoplastic, and the excess thermoplastic is scraped away from the cubes. After trimming, the steel cubes are removed and the material is allowed to cool. A heated steel cube is bonded to the thermoplastic square with an epoxide adhesive and allowed to cure before the bond strength can be determined on a dynamometer. The bond strength is determined in accordance with ASTM Test Method for Bond Strength Test for Thermoplastic Traffic Marking Materials (D 4796).
5. *Impact Resistance*—Impact resistance is determined on blocks of thermoplastic using an Izod-type impact apparatus. The procedure given in ASTM Test Methods for Impact Resistance of Plastics and Electrical Insulating Materials (D 256) is used except the specimen is not notched.
6. *Flowability*—This test is a measure of the thermoplastic marking materials' ability to flow. It is closely related to the viscosity of the material. The test involves melting a weighed sample in a pint can for 4 h with constant agitation. The can is suspended at a 45° angle, allowing material to flow over the edge until the flow ceases. The residue is weighed and the flowability is calculated. Test the material in accordance with AASHTO Test Method T-250.

Pavement Marking Tape

Film Thickness—The adhesive layer is removed from the tape with a suitable solvent, and the thickness is measured with a micrometer. The glass beads are included in this measurement, which is in contrast to films from liquid coatings where the glass beads are not included.

Reflectance and Retroreflectance—Reflectance and retroreflectance are measured in the same manner as liquid coatings. Some newer tapes are measured at a variety of illumination and observation angles because of their geometry, but the theory remains the same. For information, see No. 5 under subsection entitled "Appearance and Physical Characteristics."

Glass Bead Adhesion—A qualitative test to check glass bead adhesion is to firmly scratch the surface of the tape with a thumbnail. Acceptable adhesion for this test is when beads are not easily removed from the surface.

Tensile Strength—A 1-in.-wide strip of tape is tested in accordance with ASTM Test Method for Tensile Properties of Plastics (D 638) at a test rate of 0.25 in./min (0.64 cm/min).

Adhesive Shear Strength—The adhesive shear strength is a measure of the adhesive strength between the tape and the pavement. A 1 by 3-in. (2.54 by 7.62-cm) piece of carborundum extra course emery cloth is applied to the adhesive face of a 1 by 6-in. (2.54 by 15.24-cm) strip of tape with a 1-in. (2.54-cm) overlap. A pressure of 50 psi (35 235 kg/m) is applied to this overlapped area. The specimen is then tested in accordance with ASTM Test Method D 638 at a speed of 0.50 in./min (1.27 cm/min).

Skid Resistance—The skid resistance of tapes are measured on a British Pendulum Tester. This pendulum impact tester measures energy loss as a rubber slider travels over the specimen. The test can be used in the laboratory or in the field. The values are measured in British pendulum numbers (BPN). The test should be made in accordance with ASTM Test Method of Measuring Surface Frictional Properties Using the British Pendulum Tester (E 303).

Glass Beads

Gradation—The gradation by size of glass beads is a measure of how well a pavement marking will perform as a retroreflective media. AASHTO specification M-247 gives two gradations of glass beads. Type 1 is known as a standard gradation, and Type 2 is known as a uniform gradation. The distribution specified by AASHTO is shown in Table 1.

To perform the test, the beads are hand sieved through standard sieves starting with the largest opening and progressing through to the smallest opening sieve. The glass beads are weighed on each sieve, and the percent passing each sieve is calculated.

The test is performed in accordance with ASTM Test Method for Sieve Analysis of Glass Spheres (D 1214).

Roundness—The roundness of glass beads is another measurable indication of how well a pavement marking will perform as a retroreflective media. As mentioned earlier, only round spheres can reflect light back toward the light source.

To test for roundness, the glass beads are mechanically separated by controlled vibration of a glass plate held at a fixed slope as shown in Fig. 4. The glass spheres that are round will roll down the slope while irregular-shaped particles will vibrate to the top. After testing the complete sample, the percent rounds can be calculated by weighing the amount of spheres that have rolled down the slope. The test is performed in accordance with ASTM Test Method for Roundness of Glass Spheres (D 1155).

TABLE 1—Glass bead gradations as specified by AASHTO Standard M-247.

Sieve Designation		Mass Percent Passing	
Standard, mm	Alternate No.	Type I	Type II
0.850	20	100	. . .
0.600	30	75–95	100
0.425	40	. . .	90–100
0.300	50	15–35	50–75
0.180	80	. . .	0–5
0.150	100	0–5	. . .

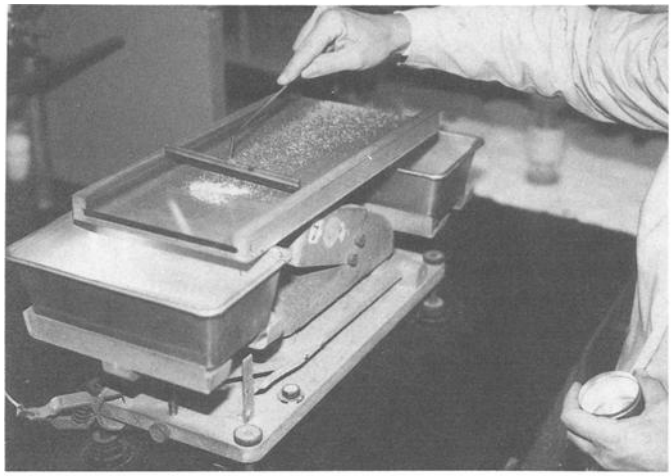


FIG. 4–Glass bead roundness apparatus.

FIG. 6–Applied test stripes.

Refractive Index—To determine the refractive index of glass beads, the beads are treated as a pigment and are tested in that manner. Most pigments are tested using the liquid immersion method (Becke Line method or equivalent) at a temperature of 25°C.

Field Evaluation of Marking Materials

Field evaluation of traffic marking materials is useful in determining the relative service life of these materials under actual road conditions using transverse lines (Figs. 5 and 6). As a guide, ASTM Method for Conducting Road Service Tests on Traffic Paint (D 713) is excellent for performing field evaluations.

FIG. 5–Field evaluation application check.

Application Process

Location For Tests—Pavements should be selected where traffic is free flowing without grades, curves, intersections, or other phenomena that would cause excessive braking or turning. The area should have uniform wear, full exposure to sunlight throughout the day, and have good drainage. Interstate highways are usually excellent choices for testing.

Wet Film Thickness Measurement—Wet film thickness is measured with a wet film thickness gage. The most popular one is a piece of metal with calibrated notches cut at various mil thicknesses as shown in Fig. 7. The gage is placed in a freshly applied line and withdrawn. The notch with the highest reading that has paint on it is the wet film thickness.

The wet film thickness is measured and adjusted before the test line is applied to the pavement. On a piece of roofing paper, place a rigid metal test panel. Apply a test line to the panel using a motorized striper. Immediately determine the wet film thickness. Adjust the pressure and repeat until the proper thickness is obtained.

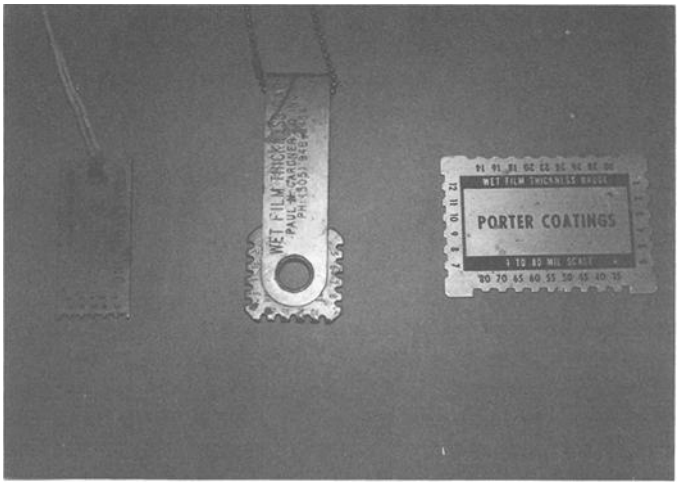


FIG. 7–Wet film thickness gages.

Film thickness for thermoplastic is usually measured on a test panel after cooling with a pair of calipers.

Glass Bead Measurement—There are two methods that can be used to quantify the weight of glass beads used. The first involves weighing a freshly applied stripe without beads on test panel and a test stripe with beads. The difference in weight is used to calculate the quantity of glass beads. This procedure is described in ASTM Method D 713.

The second procedure involves securely tying a bag around the bead nozzle of the striper and catching the beads in the bag as the striper moves over a measured distance. The weight of beads caught is determined and used to calculate the application rate for the beads.

Glass bead distribution is checked on a beaded test panel. The beads should be evenly distributed across the width of the stripe, approximately 70% of the beads should be buried in the material, and the remaining beads should be 50% embedded in the material. Nozzle pressure and angle should be adjusted until the distribution is acceptable.

Application Procedures—Before applying any test lines, wet film thickness, line width, glass bead application rate, and glass bead distribution should meet the specification. Several transverse test lines are usually applied. The first is for the Auto-No-Track Time determination (see next section). Two glass-beaded lines and one unbeaded line are usually applied. Often a test panel is placed in one of the beaded lines between the wheel tracks as a double check for line quality.

Performance Criteria

Auto-No-Track Time—The auto-no-track time is determined by passing over a freshly applied line in a standard-sized passenger car. This is usually done at 25 to 35 mph (40.25 to 56.35 km/h) at the specified no-track time. Any deposit of paint on the roadway or exposure of the pavement under the test line is considered as not meeting the no-track requirement. The laboratory no-track time described in ASTM D 711 has little or no correlation with the field results.

Appearance—This is the general condition of the test lines when viewed from a distance of 10 ft (3.05 m). It takes into consideration color, bleeding, darkening, fading, dirt collection, etc. This is done for each wheel track. A numerical value is usually assigned from 0 to 10 with 10 being the highest quality.

Durability—The durability is rated as to the percentage of material remaining on the pavement. The determination is made in each wheel track. A numerical value is usually assigned from 1 to 10 as determined by the percentage of material remaining, with 10 representing no material has worn away. ASTM Test Methods D 821 and Test Method for Evaluation Degree of Chipping of Traffic Paint (D 913) are used as guidelines.

Night Visibility or Retroreflectance—Retroreflectance measurements are made in each wheel path using a portable retroreflectometer as previously described. On the day of application, the meter reading of a beaded line is assigned a value of 10 and the reading of an unbeaded line is assigned a value of 0. Subsequent readings will be assigned a value in relation to a percentage of the original reading.

Evaluation

Periodic inspections of the test stripes are made, usually monthly. At each inspection, daytime appearance, durability, and retroreflectance values are recorded. It is good practice to obtain data during the winter season.

1. *Weighted Rating*—An excellent method to compare the relative performance of the test stripes is to assign each stripe a weighted rating. Each performance criteria that receives a rating is weighted as a percentage of the entire test. The weighting system used by the Virginia Department of Transportation is as follows:

$$R = 0.1A + 0.2D + 0.7N$$

where

R = overall weighted rating,
A = daytime appearance rating (10%),
D = durability rating (20%), and
N = retroreflectance (70%).

Other percentages can be assigned to the rating components according to the importance of the user.

2. *Length of Useful Life*—This can be defined as the projected or actual useful life in days from the day of application to the day on which the weighted rating reaches a value of 4 or if any of the rating values (appearance, durability, or retroreflectance) reaches a value of 3. If the evaluation is terminated and neither of the above is reached, the projected useful life can be calculated as follows:

$$L = D(10 - 4)/10 - R = 6D/10 - R$$

where

L = length of useful life,
D = days since application, and
R = overall weighted rating on the termination day.

3. *Weighted Cost Factor*—A weighted cost factor is useful in determining which material has the best performance at the lowest cost. It is calculated as follows

$$WCF = R[(C + AC)/L]$$

where

WCF = weighted cost factor,
C = material manufacturers price,
AC = cost to apply a given quantity of material,
L = length of useful life, and
R = overall weighted rating.

Special Considerations for Pavement Marking Tapes

Application of pavement marking tapes will vary with type of tape and manufacturer. Many tapes require primers or adhesives to be applied to the pavement before applying the marking tape. Most are rolled with a weighted roller after application to assure good contact between the adhesive and the pavement. The manufacturers directions for application should be followed closely.

In addition to the previously discussed evaluation criteria, removable tapes are also evaluated for their ability to be easily removed. About 90 days after application, a test line is removed by lifting a corner with a putty knife and pulling up the line. An acceptable tape should be removed in large sheets, not small pieces that are difficult to remove.

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Water-Repellent Coatings

by Victoria Scarborough[1] *and Thomas J. Sliva*[2]

WATER REPELLENTS ARE TRANSPARENT COATINGS formulated for the purpose of protecting porous substrates by preventing the penetration of liquid water. Unlike waterproofing materials and sealers, water repellents allow the passage of water vapor and generally are not designed to prevent the intrusion of liquid water under hydrostatic pressure.

Water is known to penetrate porous materials and contribute to their deterioration [*1–3*]. Examples include warping and swelling of wood and cracking and spalling of concrete and masonry caused by freeze/thaw cycles and dissolved salts. Further, chloride ions in deicing salts can accelerate the corrosion of reinforcing steel in concrete. Water repellents are used to provide protection against such damage.

Water repellents provide protection by depositing hydrophobic compounds on the substrate, thus modifying the surface tension of the treated area. The result is that water no longer "wets" the surface but is instead repelled. Visually, the result after the application of water repellents may be beading of water.

Composition

Most water repellents are composed of 1 to 65% monomeric or polymeric hydrophobic compounds suspended or dissolved in a carrier solvent. The products are generally classified by the type of compounds used to deliver the water repellency, e.g., acrylic, siliconate, silane, siloxane, metallic stearate, etc. The applied material may "cure" by simple carrier evaporation, or a chemical reaction may occur between the hydrophobic compounds and the substrate.

The carrier solvent used is selected based on its compatibility with the hydrophobic compounds. Organic solvent carriers can be aliphatic, aromatic, or chlorinated solvents which can be derived from petroleum distillation. These carriers are considered volatile organic compounds (VOC) and, in recent years, have been subject to restricted use by state and federal air emission control regulatory agencies. Thus, using water as a carrier in water repellents has been the focus of recent formulation efforts.

[1]Group leader, Research & Development, Thompson-Minwax, Inc., 10136 Magnolia Dr., Olive Branch, MS 38654.
[2]Assistant technical director, D/L Laboratories, 116 East 16th St., New York, NY 10003.

Classification

Water repellents can be classified as either film formers or penetrants. As film formers, the substrate pores are filled and there is a continuous film on the surface. Examples of film formers include acrylic polymers or silicone elastomers. In most cases, the film-forming portion of the water repellent is a blend of several different hydrophobic compounds.

Water repellents that are penetrants line the pores of the substrate and generally do not visibly alter the surface of the substrate. Examples include solutions of metallic stearates or paraffinic waxes. Penetrants also include reactive chemicals such as silanes and siloxanes which covalently bond to the silicate minerals in cementitious substrates. This latter reaction may be catalyzed by moisture and/or alkaline material present within the substrate.

SCHEDULE OF TESTING

Most of the major laboratory tests used for the evaluation of water repellents are outlined in the following sections: Tests on Physical Properties, Tests for Water Repellency of Treated Wood, and Tests for Application on Treated Masonry. All the tests described may not be required for each water repellent, and the selection of the tests to be conducted may be guided by the type and recommended use of the treatment or as agreed upon by buyer and seller.

Tests on Physical Properties

Typical physical properties tested on a liquid water repellent prior to application include weight per gallon, viscosity, drying time, color, flash point, pH, storage stability, percent nonvolatile content, and volatile organic compound content (VOC).

Many of these tests are outlined in Section 8 of this manual on "Physical Characteristics of Liquid Paints and Coatings" and are summarized as follows:

Weight per gallon	ASTM D 1475
Viscosity	ASTM D 1200, Ford Cup
	ASTM D 2196, Brookfield
Drying time	ASTM D 1640
Color	ASTM E 1544, Gardner
Flash point	ASTM D 56, Tag Closed Cup
pH	ASTM E 70

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Storage stability	ASTM D 2243 Freeze/Thaw
	ASTM D 1849 Heat Aging
% nonvolatiles	ASTM D 2369
	ASTM D 5095
VOC content	ASTM D 3960

Tests for Water Repellency of Treated Wood

Dimensional Stability

The relative ability of water repellents to retard dimensional changes in wood submerged in water is measured using the "wood swellometer test" and is detailed in Federal Specification TT-W-572b Par 3.7, Water Repellency [*4*]. This test compares the swelling of untreated control specimens with the swelling of treated specimens after each has been submerged in water for 30 min. Similar procedures are described in: the National Woodwork Manufacturers Association Test Method NWMA-M-2-81 [*5*]; in ASTM Test Method D 4446, "Method for Determining the Anti-Swelling Effectiveness of Water-Repellent Formulations and Differential Swelling of Untreated Wood When Exposed to Liquid Water Environments"; in American Wood Preservers Association Standard M-18, "Standard Method of Testing Water Repellency of Pressure-treated Wood" [*6*]; and in ISO/DIN 4496, "Wood Test Method-Determination of the Radial and Tangential Shrinkage" [*7*].

In Federal Specification TT-W-572b, water repellent effectiveness is measured on treated Ponderosa pine sapwood that is cut into 0.25 by 1.5 by 10-in. (6 by 38 by 254-mm) wafers. The wafers are cut from two adjacent specimens from each of five different boards. Specimen pairs of ten wafers are required to make a set for testing, one for the treated wafers and one for the untreated controls. Five wafers (one from each board) are immersed in the test water repellent for 30 s. The wafers are cured under standard conditions for four days or until constant weight is attained.

The wafers are inserted into a holding device fitted with a micrometer at one end known as a swellometer gauge. One end of the wafer touches the base of the gauge, while the other just touches the plunger dial of the micrometer. The wafer apparatus is immersed in water for 30 min, and a dial reading is made before and after immersion.

The difference between the dial reading of the treated and the untreated control wafers is divided by the dial reading of the untreated control wafers and multiplied by 100. The average of these five readings represents the water-repellent effectiveness in percent of the product. Federal Specification TT-W-572b requires that a water repellent exhibit a minimum of 60% water repellent effectiveness. ASTM Test Method D 4446 differs from the federal specification in that it requires a 3-min dipping time for water-based water repellents, and it specifies that all control untreated specimens must swell a minimum of 0.325 in. (0.8 cm).

Water Absorption

Water repellent effectiveness can also be measured gravimetrically using ASTM Test Method D 5401, "Evaluating Clear Water Repellent Coatings on Wood." Water absorption is tested by cutting matched 2 by 4 by 12-in. (50 by 100 by 305-mm) Ponderosa pine sapwood boards. Five boards are treated with the test water repellent by immersing for 30 s. Five boards serve as untreated controls. After curing the boards under standard conditions to constant weight, they are weighed, immersed in water for 30 min, and reweighed. The difference between the absorption of the treated and the untreated boards is divided by the absorption of the untreated boards and multiplied by 100. The average of the five treated boards represents the water repellent effectiveness in percent of the product.

Unlike with Federal Specification TT-W-572b, the boards used in this test can be exposed to exterior weathering cycles, returned to the conditioning room to attain constant weight, and water repellent efficiency can be determined over periodic exterior exposure intervals to determine long-term effectiveness.

Beading

Water repellents for application on wood can be evaluated for their ability to form and hold a water bead [*8*]. A suitable test is described in ASTM D 2921, "Test Method for Qualitative Tests for the Presence of Water Repellents and Preservatives in Wood Products." After the wood has been treated and allowed to cure, several water droplets are placed on the wood with an eye dropper or other device. The time required for the droplets to lose their spherical shape and flatten out is recorded. The test can be used to compare water-beading ability before and after either artificial or natural weathering. The ability to bead water does not prevent water absorption as described in ASTM D 5401, nor does it necessarily correlate with the ability to retard dimensional changes in wood as described by Federal Specification TT-W-572b.

Paintability

If wood is to be painted and a water repellent is used as an undercoat, it may be necessary to evaluate the effects of the water repellent on the primer or topcoat. Evaluations can include checking the adhesion of the topcoat to the substrate, observing any changes in color to the topcoat, and measuring the drying characteristics of the topcoat. These evaluations may also be made after a periodic weathering of the water repellent–treated surface before the topcoat is applied.

Weathering

Substrates treated with water repellents can be subjected to artificial or outdoor weathering, e.g., using ASTM G 53, "Practice for Operating Light- and Water-Exposure Apparatus (fluorescent UV-Condensation Type) for Exposure of Nonmetallic Materials," and ASTM D 4141, "Practice for Conducting Accelerated Outdoor Exposure Tests of Coatings." The substrate is evaluated for appearance properties like cracking (as shown in ASTM pictoral standards D 661, "Test Method for Evaluating Degree of Cracking of Exterior Paints"), discoloration, mold and mildew growth, and dirt pickup. The substrate may also be evaluated for beading ability or water repellent effectiveness.

Tests for Application on Treated Masonry

Water Repellency

Water repellency on masonry is determined following procedures described in Federal Specification SS-W-110c, Par.

4.3.2. [9]. Mortar cubes are prepared as described in the method. These are weighed, immersed in water, and the amount of weight gain recorded. The same cubes are dried to constant weight and then immersed in the test water repellent for 10 s. Three cubes are tested for each water repellent under evaluation.

After the water repellent has cured, the cubes are immersed in water for 72 h. The percent water absorbed by the treated cubes is calculated based on the weight of the dry treated cubes.

Chemical Resistance

The resistance of a water repellent to the intrusion of various chemicals is determined following methods modified from procedures described in: ASTM C 267, "Test Method for Chemical Resistance of Mortars"; ASTM C 67, "Method of Sampling and Testing Brick and Structural Clay Tile"; Report 244 of the National Cooperative Highway Research Program, "Concrete Sealers for Protection of Bridge Structures" [*10*] and ASTM C 672, "Test Method for Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals." Mortar cubes are prepared and then treated, cured, and immersed in a specified chemical solution. Uncoated control cubes are included in the immersion. Typical chemicals used in this test include fuels and oils, various salt solutions, and acid and alkaline solutions.

Differences in weight gain or loss over time are measured and plotted as compared to the untreated control. The rate of weight gain or loss over time during immersion may be more significant than the actual difference. By charting the weight gain or loss over time, the rate of deterioration may be determined.

Chloride ion penetration resistance is of particular interest in testing for the resistance of water repellent–treated masonry since reinforcing steel in concrete will corrode and deteriorate after prolonged exposure to salt. A method of determining the resistance of concrete to chloride ion penetration is described in the AASHTO Method T 259 [*11*].

Freeze/Thaw Resistance

Freeze/thaw resistance is determined by methods modified from procedures outlined in ASTM C 67, mentioned above and ASTM C 666, "Test Method for Resistance of Concrete to Rapid Freezing and Thawing." Treated cubes are subjected to cycles of freezing and thawing, and the amount of water absorbed and the change in absorption with time is determined. The cubes are evaluated for weight loss and physical deterioration such as cracking and spalling after each series of cycling.

Moisture Vapor Transmission

Because the passage of moisture vapor through masonry may affect the long-term performance of a structure, water repellents applied to that structure may be required to demonstrate their ability to allow the passage of moisture vapor. Several methods are available to measure moisture vapor transmission of the applied film and include ASTM D 1653, "Test Method for Water Vapor Transmission of Organic Coating Films," and ASTM E 96, "Test Methods for Water Vapor Transmission of Materials." Generally, these methods measure the rate at which water vapor passes through a coating film. The specimen is sealed to the open mouth of a cup or dish containing desiccant, and the assembly is placed in a test chamber with a controlled atmosphere. The cup or dish is exposed to a specified relative humidity, and periodic weighings are made to determine the rate of water vapor through the film. Another method is described in NBS Technical Note 883, Par. 2.2.2, "Moisture Vapor Transmission on Brick" [*12*] which measures the moisture vapor transmission of the treated brick rather than the film.

Efflorescence

Efflorescence is a crystalline deposit on the surface of masonry which is whitish in appearance and often detracts from the appearance of the substrate. Water repellents may be used to prevent the formation of efflorescence. Their efficiency at preventing efflorescence can be measured using the method described in NBS Technical Note 883, Par. 2.2.3. [*12*].

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[*4*] "Water Repellent for Use on Wood," General Services Administration, Federal Specification TT-W-572b, Washington, DC, May 1969.

[*5*] National Woodwork Manufacturers Association, NWMA Swellometer Test, "Standard Method for Determining the Water-Repellent Effectiveness of Treating Formulations," NWMA-M-2-81.

[*6*] American Wood Preservers' Association, Stevensville, MD, *AWPA Book of Standards*.

[*7*] ISO test methods can be obtained in the United States from ANSI, 11 W. 42nd Street, New York, N.Y. 10036.

[*8*] Kalnins, M. A. and Katzenberger, C., "Wettability and Water Repellency of Wood: A Faster, More Convenient Method of Measurement," presented at the Second Cellucon Conference, Wrexham, Wales, UK, July 1986.

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[*11*] Standard Specifications for Transportation Materials and Methods of Sampling and Testing, Part 2, Method T 259-78, American Association of State Highway and Transportation Officials, Washington, DC.

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Part 14:
Analysis of Paints and Paint Defects

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Analysis of Paint

by Darlene Brezinski[1]

SAMPLING

The importance of appropriate sampling for analytical work cannot be overemphasized. Unfortunately, this topic is often not given sufficient thought, and there is often not enough training on the subject. A clear understanding of the nature of the problem or the reason analysis is needed must be established prior to obtaining a sample. It is extremely important to know the compositional makeup of the bulk material from which the sample is being taken. Without this knowledge, improper sampling can very easily occur. The homogeneity or heterogeneity of the sample along with its stability is very important to consider. The composition of a sample may change once it is removed from its natural matrix or environment due to interactions with a container, ultraviolet light, or air, for example. One should also know in advance what level of precision is required of the analysis and what compositional information is required.

Development of a sampling plan is one of the most important steps in providing reliable samples and consequently accurate and reliable data. The types of samples usually encountered are:

Representative Sample: A sample considered to be typical of the bulk material and whose composition can be used to characterize the bulk with respect to the parameter measured.

Systematic Sample: A sample taken according to a systematic plan with the objective of investigating systematic variability of the bulk. Systematic effects due to time or temperature are typical matters of concern.

Random Sample: A sample selected by a random process to eliminate questions of bias in selection and/or to provide a basis for statistical interpretation of measurement data.

Composite Sample: A sample composed of two or more increments that are combined to reduce the number of individual samples needed to average compositional variability [*1*].

There are basically three kinds of sampling plans that can be used in a measurement process. Intuitive sampling plans may be defined as those based on the judgment of the sampler. General knowledge of similar materials, past experience, and present information about the bulk material, ranging from knowledge to guesses, are used in devising such sampling plans. Because the samples are based on judgement, only judgmental conclusions can be drawn when considering the data. In the case of controversy, decisions on acceptance of conflicting conclusions may be based on the perceived relative expertise of those responsible for sampling [*1*].

Statistical sampling plans are those based on statistical sampling of the bulk materials and ordinarily can provide the basis for probable conclusions. Hypothesis testing can be involved, predictions can be made, and inferences can be drawn. Ordinarily, a relatively large number of samples will need to be measured if the significance of small apparent differences is of concern. The conclusions drawn from such samples would appear to be noncontroversial, but the validity of the statistical model used could be a matter of controversy [*1*].

Protocol sampling plans may be defined as those specified for decision purposes in a given situation. Regulations often specify the type, size, frequency, sampling period, and even location and time of sampling related to regulatory decisions. Not specifically following any part of the protocol could be reason for discrediting a sample. The protocol may be based on statistical or intuitive considerations but is indisputable once established [*1*].

When decisions are based on identifying relatively large differences, intuitive samples may be fully adequate. When relatively small differences are involved and the statistical significance is an issue, statistical sampling will be required [*1*].

General Sampling Techniques

It is obvious that the sample submitted for analysis must accurately reflect the bulk material from which the sample was taken. Personnel taking samples should be trained in proper protocol for obtaining samples from bulk material. Equally as important as training is the use of proper containers necessary for storing samples. Many types of containers can alter the integrity of the sample. A paint sample submitted in the original container is not necessarily a representative sample as often volatile components have already been lost or the contents have been adulterated. Assumptions regarding the integrity of the sample are extremely difficult to make, and good analysts need to constantly bear in mind the history of the sample itself.

Detailed procedures regarding sampling of all sorts of coatings would be impossible to write; however, ASTM Practice for Sampling Liquid Paints and Related Pigmented Coatings

[1]Consolidated Research, Inc., 200 E. Evergreen Avenue, Mount Prospect, IL 60056.

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(D 3925) and ASTM Method for Sampling Industrial Chemicals (E 300) should be examined for detailed recommendations.

All the precision in weighing, measuring, calculating, and so forth has absolutely no meaning if the sample is not a valid and representative sample. The sample taken for analysis must totally and accurately reflect the composition of the bulk material from which it was taken. If there is any doubt about the integrity of the sample *as a representative sample*, the analysis should not be conducted as the data has no meaning. This becomes extremely important when dealing with samples where the bulk is large and perhaps not always completely homogenous [*1*]. In the real world of sampling, it is often very difficult to even know if the sample was obtained properly and if it is representative. The analyst usually has no control over the sampling step itself. In these cases, it becomes important for the analyst to stress that the data are only representative of the sample which has been analyzed and not necessarily representative of the bulk. Rather serious management decisions can be falsely made if the decision is based on data which is not representative data.

Care should be taken to assure that all containers, agitators, and sampling apparatus are clean and that they can in no way contribute to contaminating the sample. Reusable syringes in particular can pose problems, particularly in trace analysis, if they are not cleaned extremely well. Contaminant materials will lead to erroneous test results as the contaminate will be assumed part of the sample. For pigmented coatings which are dispersions, finely divided pigment particles may settle upon standing. Consequently, very thorough agitation is necessary at every stage of the sampling and analysis procedure.

Airtight storage containers are necessary to prevent evaporation of sample material. Volatile solvents may also diffuse through the walls of plastic containers. The loss of volatiles subsequently introduces significant error in such tests as viscosity, weight per gallon, and nonvolatile content. If cap liners are used for samples, they must be made of a nonreactive material. It is also very important in all stages of sampling/analysis that the samples be kept at fairly constant and consistent temperatures. Extremes of temperatures may change the properties of some coatings.

Proper labeling of the sample cannot be stressed enough. Labeling should be done in accordance with prior established standard operating procedures (SOPs) for the laboratory. The more information available on the label, the less likely error will be introduced either in the handling of the sample or in the analysis. Formula composition, if known, can be an asset to the analyst in choosing the best analytical methods and save valuable and costly analytical time.

Laboratory Protocol

The analytical laboratory today must have standard operating procedures (SOPs). This is standard, acceptable practice today, and laboratories that have not implemented these procedures will find it more difficult to maintain credibility of the data with their clients. Standard operating procedures define clearly how each step of the laboratory operates. Clear SOPs are necessary for training, logging samples, calibration, quality assurance, receipt of samples, chain-of-custody, report formats, analytical methods, handling of hazardous materials, etc.

Whatever kind of sampling plan is developed, it should be written as a protocol containing procedures (SOPs) that must be followed. It should address the following:

- when, where, and how to collect samples
- sampling equipment, including its maintenance and calibration
- sample containers, including cleaning, addition of stabilizers, and storage
- criteria for acceptance and/or rejection of samples
- criteria for exclusion of foreign objects
- sample treatment procedures such as drying, mixing, and handling prior to measurements
- sub-sampling procedures
- sample record keeping such as labelling, recording, and auxiliary information
- chain of custody requirements [*1*]

Appropriate laboratory protocol has established SOPs in place for every facet of the operation. Sample control has to include not only the receipt and handling of the sample but the handling and storage of the data.

Implementation of a chain-of-custody plan for each sample is most critical to good operating practices in the analytical lab today. It provides traceability for the sample upon receipt and distribution of the sample for analysis. The purpose of chain-of-custody is to ensure control of the sample and corresponding data and that the data are verifiable. The flow of samples for analysis and the associated paper must be clear to everyone involved in the laboratory.

Analytical Quality Assurance

The validity of analytical data must be clearly established through the documentation of quality assurance practices. This is particularly important because often analytical determinations and the subsequent data may be used as evidence in a court of law. Standard operating procedures should be established and encompass the following: record keeping, sample homogeneity, calibrations, reference standards, calculations, laboratory housekeeping, the statistics of interlaboratory studies, and practical quality control.

Laboratory accreditation is becoming increasingly important in today's environment to provide a level of confidence in the laboratories' capabilities, personnel, testing procedures, and equipment. It establishes integrity and reliability in the testing and the data. As regulatory requirements become more demanding, the nature of the analytical methodology has been changing to more sophisticated analyses and, along with these changes, there has been an increased emphasis on quality assurance (QA) and quality control (QC). Successful laboratories have made major commitments to quality products and quality data. Therefore, the process of verification of laboratory procedures is becoming more important for providing precise and accurate data.

GENERAL TESTING

Before any tests are run on the coating and prior to separation, testing to establish some basic parameters or con-

formance properties should be run. Among these are: flash point, density, water content, nonvolatile content by weight and/or volume, and pigment or ash content. Reference should be made to elsewhere in this manual for more information regarding determination of density, specific gravity, and so forth.

Flash Point

The flash point of a material is defined as the lowest temperature, corrected to a pressure of 760 mm Hg (101.3 kPa, 1013 mbar) at which application of an ignition source causes the vapor of the specimen to ignite under specified conditions of test. Flash point is one of the properties used to classify liquids according to their flammability by governmental regulatory agencies. Several different flash point methods are available. The analyst must determine which one of these methods is appropriate for the sample to be analyzed and then follow the recommended ASTM procedures. Both Tag open cup and closed cup methods, Pensky-Martens closed cup, and Setaflash tester methods are commonly used in the coatings industry. [ASTM Test Method for Flash Point and Fire Points of Liquids by Tag Open-Cup Apparatus (D 1310); ASTM Test Method for Flash Point by Tag Closed Tester (D 56); ASTM Test Methods for Flash Point by Pensky-Martens Closed Tester (D 93); ASTM Test Methods for Flash Point of Liquids by Setaflash Closed-Cup Apparatus (D 3278)]. Laboratories need to be certain of the shipping requirements and the appropriate methods prior to analysis of the sample.

Density

Density is weight per unit volume. It is a key property in the identification, characterization, and quality control of a wide range of paint materials. The density of water at various temperatures is used to calibrate the volume of the container. The weight of the paint liquid contents of the same container at the standard temperature is then determined and density of the contents calculated in terms of grams per milliliter, or pounds per gallon, at the specified temperature.

Density measurements in terms of weight per gallon are commonly used to check paint quality. If the density is not within specification, there is a good chance that there was a mischarge or other serious problem. This could indicate further chemical analysis is required to determine the nature of the problem. ASTM Test Method for Density of Paint, Varnish, Lacquer, and Related Products (D 1475) is suitable for the determination of density of paint and related products and components when in liquid form.

ASTM D 1475 provides for the maximum accuracy required for hiding power determinations. Automatic equipment for measuring density is available from several manufacturers [see ASTM Test Method for Density and Relative Density of Liquids by Digital Density Meter (D 4052)]. For higher precision if working with nonpigmented materials, ASTM Test Method for Specific Gravity of Drying Oils, Varnishes, Resins and Related Materials at 25/25°C (D 1963) can be used to determine specific gravity and the corresponding density.

Water (Content) Determination

Control of water content is often important in controlling the performance of paint and paint ingredients and is certainly critical in determining and controlling the volatile organic compound (VOC) content. ASTM Test Method for Water in Paints and Paint Materials by Karl Fischer Method (D 4017) is applicable to all paints and paint materials, including resins, monomers, and solvents, with the exception of aldehydes and certain active metals, metal oxides, and metal hydroxides. The Karl Fischer Method has been evaluated for pigmented products containing water in the 30 to 70% range; however, it is believed that the method is also applicable for higher and lower concentrations. The method consists of dissolving the sample in pyridine, or other appropriate solvent, and titrating directly with standardized Karl Fischer reagent to an electrometric end point.

ASTM Test Method for Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph (D 3792) is also used for determining water in many latex systems. That method has not been evaluated for other water reducible paints, but is believed to be applicable. The established working range of the method is from 40 to 55% water, but there is no reason to believe that it will not work outside of this range. In this method, a suitable aliquot of whole paint is internally standardized, diluted, and injected into a gas chromatograph. By choosing the correct column and conditions, water can be separated from the other volatile components.

Water content in pigments may be determined in accordance with ASTM Test Methods for Common Properties of Certain Pigments (D 1208).

SEPARATION OF SOLIDS AND VOLATILE CONTENT

Separation of solids is routinely performed for determining the percent composition of the coating, i.e., % NVM (nonvolatile materials), % pigment, and % solvent. In many cases, however, separation of these materials is also necessary for further identification purposes, to check formulation related problems, and for general problem solving.

Nonvolatile Content by Weight

Nonvolatile measurement is one of the most widely used tests for coatings characterization. It determines the quantity of coating remaining after all solvents or water and other volatiles have been removed. When used in conjunction with volume nonvolatile content, the area covered by a gallon of paint or coating can be determined.

It has become customary to determine the amount of nonvolatile material, or solids, in a coating and that information is useful to producers, users, and to environmental and health and safety interests in comparing the coverage of competing products and in estimating the volatile organic content. Standard practice has been to accurately weigh by difference from a syringe a small sample of paint into a tared aluminum foil, flat-bottomed dish. The dish is heated for a specified temperature and time (usually to constant weight at 105°C), cooled in

a desiccator, and weighed. From this weight and the original weight of the empty dish the weight of nonvolatile material may be calculated. The procedure is not as simple as it first appears, and different types of coatings require different methods. ASTM Guide for Determining Volatile and Nonvolatile Content of Paint and Related Coatings (D 2832) is intended to aid in the selection of the proper standard for determining the volatile and nonvolatile content of coatings. This guide should be examined carefully and followed prior to determining nonvolatile content.

Perhaps the most commonly used method is ASTM Test Methods for Volatile Content of Coatings (D 2369). This method is the procedure of choice for determining the volatiles in coatings for the purpose of calculating the volatile organic content (VOC) in coatings. Correspondingly, the nonvolatile (NVM, or solids) is used to determine the weight percent solids content.

Another commonly used procedure is ASTM Test Method for Nonvolatile Content of Latexes (D 4758). This method should not be used for determining VOC of formulated coatings; however, it is appropriate for obtaining the weight percent of a commercial latex product that, when incorporated into a coating product, constitutes the binder content of the coating.

The nonvolatile content of resin solutions is useful to coatings producers and users for the determination of the total solids available for film formation and for the estimation of VOC. ASTM Test Methods for Nonvolatile Content of Resin Solutions (D 1259) provides the detailed procedures.

Nonvolatile Content by Volume

A measure of the volume of dry coating obtainable from a given volume of liquid coating is considered by some to be a better measure of value than percentage of nonvolatile matter by weight. ASTM Test Method for Volume Nonvolatile Matter in Clear or Pigmented Coatings (D 2697) is applicable to the determination of the volume of nonvolatile matter (volume solids) of a variety of coatings. This method is intended to provide a measure of the volume of dry coating obtainable from a given volume of liquid coating. This value is useful for comparing the coverage (square feet of surface covered at a specified dry film thickness per unit volume) obtainable with different coating products.

The value obtained may not be equal to that predicted from simple additivity of the weights and volumes of the raw materials in a formulation. One reason is that the volume occupied by a solution of resin in solvent may be the same, greater, or less than the total volume of the separate ingredients: such contraction or expansion in resin solutions is governed by a number of factors, one of which is the extent and direction of spread between solubility parameters of the resin and solvent. The spatial configuration of the pigment particles and the degree to which the spaces between the pigment particles are filled with the binder also affect the volume of a dry coating formulation. Above the critical pigment volume concentration, the apparent volume of the dry film is significantly greater than theoretical due to the increase in unfilled voids between pigment particles. The use of volume nonvolatile matter values in such instances should be carefully considered as the increased volume is largely due to air trapped in these voids.

In the method, the weight and volume of a stainless steel disk are determined. After the disk is coated with the material being tested, the weight and volume of the disk plus dried coating is determined by weighing in air and then by weighing in a liquid of known density, the volume being equal to the quotient of the weight loss of the coated disk (due to the Archimedes buoyancy effect) divided by the density of the liquid displaced. The liquid may be water or an organic liquid, such as low solvency mineral spirits, depending on the nature of the coating being tested. From the measured weights and volumes of the disk before and after coating, the weight and volume of the dried coating film are calculated. Based on the density of the liquid coating and the weight percent nonvolatile matter, the volume of the liquid coating deposited on the coated disk is calculated. The volume of the dried coating divided by the volume of liquid coating, multiplied by 100, provides the volume percent nonvolatile matter in the total liquid coating.

Pigment Content

For most water emulsion paint systems, the pigment content (often called ash) is most often determined following the determination of the weight percent nonvolatiles. ASTM Test Method for Pigment Content of Water-Emulsion Paints by Low Temperature Ashing (D 3723) covers a procedure for the pigment content determination. After weighing the dishes for NVM, the dishes are transferred to a muffle furnace and heated at a low ashing temperature of about 450°C for 1 h. Of course the analyst must keep in mind that the method is only applicable to pigments that do not decompose or lose weight at temperatures below 500°C. This would include most metal oxides, silicates, and a majority of anhydrous inorganic salts.

A note of caution is advised as this may be too low an ashing temperature for some paints. Each system is different, and one cannot assume that this temperature will be sufficient.

To separate pigment from solvent-based paints, ASTM Test Method for Determination of the Pigment Content of Solvent-Reducible Paints by High-Speed Centrifuging (D 2698) should be followed. Also ASTM Test Method for Pigment Content of Solvent-Reducible Paints (D 2371) provides a centrifugation method for separation of pigment from the vehicle.

Vehicle Separation

Separation of the vehicle from the pigment in solvent-reducible paints is desirable and often required in order to further characterize paint vehicles by chemical or instrumental methods of analysis. ASTM Standard Practice for Separation of Vehicle from Solvent-Reducible Paints (D 2372) covers the procedure for separating the vehicle from the pigment by centrifugation.

Solvent Separation

If it is desirable to separate the solvents from the vehicle, ASTM Standard Practice for Vacuum Distillation of Solvents

From Solvent-Reducible Paints for Analysis (D 3272) details a vacuum distillation procedure. For analysis purposes, however, most people prefer direct injection of paint sample into the gas chromatograph for solvent identification.

Sample Preparation

For many types of analysis, the previously discussed separation techniques are sufficient. Many chemical analyses require further sample treatment in the form of either extractions or digestions. The standard analytical techniques are always applicable in these cases. Extractions are often more attractive techniques for separating inorganic species than precipitation methods which are more time consuming. Of course the extent to which inorganic and organic species distribute themselves between two immiscible solvents differs greatly depending on the species and the extraction solvents.

Decomposition of the organic material for further analysis requires rather drastic sample treatment and typically involves oxidation techniques. Wet ashing makes use of liquid oxidizing agents such as sulfuric, nitric, and perchloric acids. Dry ashing usually implies ignition of the organic compound in air or in a stream of oxygen.

Sample dissolution is one of the most common operations in analytical chemistry. Because most quantitative techniques require that samples be introduced in liquid form, thousands of sample dissolutions are performed every working day in analytical laboratories. Despite the importance and widespread applicability of sample dissolution, most conventional digestion procedures are tediously labor-intensive, and a number of them, such as perchloric acid digestion, are potentially hazardous to laboratory personnel [*2*].

New microwave dissolution techniques make it possible to speed the preparation of solid samples by combining the rapid heating ability of microwave energy with the advantages inherent in the use of sealed digestion vessels. Researchers have found microwave dissolution to be faster, more controlled, more elegant, and more amenable to automation than conventional open-beaker or closed-vessel techniques [*2*].

The advantages of microwave dissolution include faster reaction rates that result from the high temperatures and pressures attained inside the sealed containers. These containers are made of polymers that will not contaminate or adsorb the sample and do not absorb microwave energy. The caps are designed to safely vent container gas in case of excess internal pressure buildup [*2*].

The use of closed vessels also makes it possible to eliminate uncontrolled trace element losses of volatile molecular species that are present in a sample or that are formed in the course of dissolution. Such losses can easily destroy the integrity of a measurement. In the field of elemental analysis, significant percentages of elements such as arsenic, boron, chromium, mercury, antimony, selenium, and tin are lost at relatively mild temperatures with some open-vessel acid dissolution procedures. Several of these elements have already been shown to be retained when closed vessels are used [*2*].

Another advantage of closed vessels is a decrease in blank values as compared to open-beaker work because contamination from the laboratory environment is lower and smaller quantities of reagents are used. The blank value incurred in sample preparation is an important parameter because it frequently determines the limit of detection [*2*].

CHARACTERIZATION AND CHEMICAL ANALYSIS

Analytical Data

The reporting of analytical data is exceedingly important, and every effort must be taken to ensure that the data are sound, defensible, and meaningful. Most basic texts on analytical chemistry discuss the appropriate statistical methods used in dealing with data, standard deviation etc., as well as significant figures. An excellent text by Taylor [*1*] deals with all aspects of chemical measurements and should be examined thoroughly by all analysts. Also available is ASTM Procedure for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-level Data (D 4210).

In the analytical laboratory, a method of measurement (procedure) is usually followed which specifies the equipment, reagents, sample handling, etc., and the instructions to be followed. The analyst who carries out the method is following what is called a measurement process. The most important attribute of a measurement process is whether it can be made to run in a state of "statistical control." Although repetition of measurement is subject to variability, the achievement of statistical control implies that the statistical properties of this variability are uniform over time, so that it becomes meaningful to use measurements over a limited time span to predict limits of variation for both those and future measurements and to assign the level of confidence to be associated with the limits. To achieve statistical control, all assignable causes of significant variation are removed from the process [*3*].

Given the existence of statistical control, the two most important other attributes of the process are generally the precision and the accuracy of the results. Precision is universally considered to be the mutual agreement of individual measurements about some mean value (not necessarily the true value), while accuracy refers to the degree of agreement of individual measurements with some true or accepted reference value of the property being measured. When the mean value is not identical with the reference value, the systematic difference is called the bias. We should avoid using the terms accuracy and bias interchangeably; accuracy has to do with the difference between individual measurements and some reference value, while bias represents the systematic difference between the process mean and the reference value [*3*].

Structural Analysis

All aspects of coatings manufacture, from the screening of raw materials to finished product quality assurance, depend on analysis data. The ultimate goal of analyses is to identify the chemical species contained in a sample and then determine the amount of each species. As such, both qualitative (what) and quantitative (how much) analyses must be performed. It is extremely important to try and obtain all the background information regarding the sample to be analyzed

as this information can often save time and expensive analysis costs.

Organic Structural Analysis

A. Instrumental Methods

Spectroscopy is the study of the interaction of electromagnetic radiation with matter, that is, the interaction of wavelengths of visible light, infrared light, ultraviolet light, X-rays, and radio waves and their effect on chemical substances. Spectroscopy allows the study of these effects with instruments which give an enormous amount of information in a short period of time with less stringent sample requirements than is needed with classical chemical techniques. All of the wavelengths in the ultraviolet, visible, and infrared regions provide valuable information about the structural makeup of molecules.

Infrared Spectroscopy (IR) provides a unique fingerprint useful in the identification of a wide variety of chemical species [*4*]. Certain infrared wavelengths are absorbed in the sample by the bonds between the atoms, and the absorbance is measured and plotted as a function of wavelength. Since each chemical material has its own particular and unique arrangement of atoms and bonds, its absorbencies are slightly different from those of all other chemicals.

Normally specific functional groups will give characteristic absorbencies, and these groups can be recognized. Thus, there are very specific absorbencies for groups such as carbonyls, amines, alcohols, nitro groups, and isocyanates. Although it may not always be obvious from a spectrum which chemical is being examined, the analyst will recognize these functional groups and know something about the chemical structure.

In addition, IR can be a very valuable tool for: reaction kinetic studies, hydrogen bonding, dipolar attractions and solute-solvent interaction studies, examination of the nature of hydration and the nature of inorganic lattices at various temperatures, and for studying the surface of a material by attenuated total reflection (ATR) and variation of composition with depth by variable angle ATR. These are but a few of the numerous applications of IR in the coatings field [*4*].

If more detailed information is desired and if the sample has some degree of solubility, then *nuclear magnetic resonance* (NMR) analysis can be extremely valuable. NMR spectrometry not only provides information regarding the functional groups which are present but it also provides information about the location of those functional groups relative to each other. In other words, the placement of the functional groups in the molecule can be discerned from NMR data [*5*].

If the compound is volatile and has some degree of thermal stability, *gas chromatography* (GC) can be very useful for identification purposes as well as for determining purity/impurities of materials. If a material is identified qualitatively by GC, then that material can be further analyzed quantitatively. If the compound is not very volatile or is unstable under GC conditions it may be possible to analyze it by *high performance liquid chromatography (HPLC)*. Here, as in GC, both qualitative and quantitative determinations can be made [*5*].

For both GC and HPLC, if the peak of interest can not be readily identified, it can be trapped and further analyzed by either IR or NMR techniques. Current instrumentation allows the analysis of materials like this quite readily by offering instrument capabilities such as the following: HPLC-MS, GC-IR, and GC-MS (mass spectrometry). These instruments allow accurate separation of components followed by subsequent identification.

Mass spectrometry can be applied to the quantitative analysis of organic, organometallic, inorganic and ionic compounds and materials including metals, and alloys. It is used both to confirm the presence of known compounds and to identify compounds of unknown structure. Volatile or gaseous samples, usually organic compounds, can be examined using electron impact (EI) or chemical ionization (CI) to give positive or negative ion mass spectra. Nonvolatile samples can be examined by fast atom bombardment (FAB) or thermospray ionization for inorganic and organic salts, while plasma discharge ionization is used for metals and refractory materials.

The value of mass spectrometry, of course, is absolute identification of either known or unknown compounds, particularly when combined with information from other spectroscopic techniques. Pyrolysis can also be carried out prior to ionization inside the spectrometer and thus used for characterizing both linear and cross-linked polymers.

Raman spectroscopy [*5*] is used to determine molecular structures and compositions of organic and inorganic materials. Raman, like infrared, provides characteristic frequencies of various functional groups. However, since the selection rules governing the allowable transitions are different, some frequencies may be observed in the Raman spectrum which do not appear in the infrared and vice versa. Some applications include:

- Examination of aqueous solutions of inorganic compounds. While water gives rise to intense absorptions in the infrared, making unavailable major regions of the spectrum for identification purposes, it is a poor Raman scatterer, thereby allowing the observation of vibrational transitions in the regions obscured in the infrared.
- Structural identifications of water-soluble organic compounds such as amino acids.
- Detection of weak infrared frequencies, such as the stretching vibrations of the following groups:

  —C≡C—, —C=C—, —S—S—, —C—S—, —N=N—, and —O—O—

- Determination of configurational isomers in both the solid and liquid state [*4*].

B. Chemical Methods

The techniques used in chemical analysis are of two general types: gravimetric and titrimetric. In a titrimetric analysis, the volume of known solution required to completely react with a functional group is measured. This volume is then related to the concentration of reacting species in the sample. The primary criteria for titrimetric analyses are that the sample be soluble in a suitable solvent and a reagent is found which fully reacts with the species of interest. Determination of acid, hydroxyl, and oxirane functional groups, as well as elemental analysis for nitrogen content, utilize titri-

metric techniques. Titrimetric analyses are quite sensitive, and measurements of concentration at the 0.1% level are routine. During gravimetric measurement, the weight of material formed during analysis is used to determine the composition of the original sample.

Classical chemical analyses can be further divided into two categories depending upon the type of information desired: functional group determination and the measurement of elemental composition.

The presence of functional groups in polymers and coatings can normally be determined using a combination of chemical and instrumental measurements. Building upon qualitative functional group information obtained from spectroscopic techniques, quantitative analysis can begin. In some cases specific chemical tests are also required to confirm the presence of species indicated by other techniques. The quantitative measurement of the following chemical species is routinely performed in the laboratory:

Acid (mg KOH/g sample) $COOH + KOH \rightarrow COO^-K^+$
Amine (meq/g sample) $NH_2 + HCl \rightarrow NH_3 + Cl^-$
Hydroxyl (mg KOH/g sample)
Epoxy or oxirane (meq/g or g/eq)
Isocyanate (%)
Acrylate (%)
Olefinic unsaturation
Thiol or mercaptan (meq/g) $SH + Ag^+ \longrightarrow S\text{-}Ag + H^+$

Many of the above are chemical functional groups that may be part of a large molecule or polymer. The level of these species provides information regarding a polymer or coating. For example, many of the polymers used in coatings are formed using multi-step reactions, and the reactions are monitored by functional group analysis. In addition to monitoring polymerization processes, the levels of species in coatings is of importance. When two coatings components are designed to be blended prior to application, functional group determination is needed to insure that the components are mixed in proportions which give optimum physical and durability properties.

Inorganic Structural Analysis

A. Instrumental Methods

Most inorganic compounds are not sufficiently volatile or soluble to allow identification by either gas or liquid chromatographic techniques. *Ion Chromatography* can, however, play a major role in inorganic analysis. *Infrared* analysis (*IR*) is notable for pigment identification as is discussed in a subsequent section.

X-ray Fluorescence (XRF) [5] and other emission techniques are used for elemental analysis of inorganic compounds. *X-ray Diffraction (XRD)* analysis [5] is an important tool not only in compound identification but in identifying crystal structures and in crystalline phase analysis.

Thermal analytical techniques such as *differential thermal analysis (DTA), differential scanning calorimetry (DSC)*, and *thermal gravimetric analysis (TGA)* are all used on a routine basis for identifying and analyzing inorganic compounds, as well as organic compounds. These techniques provide information about the melting points, other phase transition temperatures, and thermal stability of both inorganic and organic compounds. Also, particle size, surface area, and porosity analyses provide useful characterization information about inorganic materials [6].

Inductively coupled argon plasma spectroscopy (ICAP) [5] allows the determination of numerous elements in aqueous and organic solvent solutions. ICAP methods rely on the emission of light by atoms in the sample as opposed to the absorption of light, the principle behind atomic absorption (AA) spectrometry. Liquid and/or solid samples are readily analyzed using ICP techniques after appropriate sample preparation steps are taken. ICP analytical procedures employ classical sample preparation methods such as acid digestion, fusion, dry ashing, dilution, and extraction. In practical applications, AA and ICP are quite similar. The major differences are the speed with which ICP handles samples and most importantly its relative freedom from interferences. The technique is desirable for: quantitative determination of trace elements in aqueous and organic solvent solutions, quantitative analysis of pigments in paints and coatings, evaluation of waste materials and total metals content, and detection of trace metallic impurities in polymers.

The surface upon which a coating is deposited plays an important role in the protective properties of a coating system. A single molecular layer of oily contamination can interfere with proper bonding and result in coating adhesion failure. In addition, the oxide layer that forms in a clean metal surface is often mechanically weaker than the bulk of the metal. Under stress, this layer may flake off and carry with it the coating. Techniques for the examination of surfaces may take many forms, but all involve bombarding the sample with atomic or subatomic particles. The bombardment excites the surface of the sample, releasing energy, which can be used to determine elemental or molecular composition. Depending on the technique chosen, the "surface" examined will vary between the first several atomic layers of a sample down to the first several micrometers.

Electron beam X-ray analysis (microprobe) is one of the capabilities generally included with a *scanning electron microscope (SEM)* [5]. High-energy electrons that strike a sample during the image forming process interact with the atoms comprising that surface. Among the species formed during this interaction are X-rays having specific energies depending on the elements present in the sample. Once detected and analyzed, X-ray spectra can yield information on the elemental composition of the sample, as well as indicate the quantity of each element present. Two types of X-ray detectors are in general use. The energy dispersive detector is useful for detecting elements above sodium in the Periodic Table but is not suitable for low-level quantitative analysis. A wavelength dispersive detector observes all elements more massive than carbon and has significantly improved quantitative analysis capabilities. An instrument that contains all the imaging ability of the SEM and has full quantitative analysis capability is called a microprobe. This instrument has sufficient resolution to allow the elemental analysis of a particle less than 1 μm in diameter. The primary disadvantage of the microprobe is that X-rays can emerge from atoms several micrometers below the surface of the sample. Consequently, the signal from a thin layer of surface contamination can be lost in the signal from the substrate.

Ion scattering spectrometry (ISS) and *secondary ion mass spectrometry (SIMS)* techniques involve bombarding the sam-

ple with gas ions and analyzing the products removed from the surface [5]. Both methods exhibit very high sensitivity for all elements, including hydrogen, and can analyze a few atomic layers of exposed surface at a time. Resolution is normally on the order of millimeters with the exception of specialized instruments known as microprobes. These techniques are very useful for hazing and chalking problems where very minute amounts of material cause appearance problems at the surface of the coating. ISS and SIMS readily determine the nature and extent of the contaminating material. Cases of substrate contamination leading to adhesion problems are also more easily solved using the data provided by these analytical methods.

Electron spectroscopy for chemical analysis (ESCA) and *scanning auger microscopy (SAM)* are techniques in which a sample is irradiated with a beam of X-rays (ESCA) or electrons (SAM) to liberate electrons from the top 2 to 5 nm of the surface [5]. The energy of the liberated electrons is then analyzed to provide information regarding the composition of the surface layers in the sample. In addition to elemental composition, information can be obtained on the chemical environment of the elements present on the surface. Through comparison of spectral fingerprints with the spectra of standard materials or a library of reference spectra, compounds present on the surface can be readily identified. ESCA has the capability of observing particles approximately 1 mm in diameter and is well suited to paint films on a variety of substrates. SAM has the ability to study much smaller particles (approximately 0.2 μm in diameter), but the surface must be conductive, limiting its utility to metal surfaces.

B. Chemical Methods

In conjunction with titrimetric and gravimetric measurements, analysis of elemental composition provides important information on coatings systems. Among the many elements determined are: carbon (%), hydrogen (%), nitrogen (%), sulfur (%), chlorine (%), bromine (%), phosphorous (ppm).

The level of nitrogen in an industrial coatings system is an important analytical value because nitrogen is present in melamine, urea, and benzoguanamine oligomers, which are used as cross-linking agents in many coatings. Correct levels of cross-linking agent are essential since physical, chemical, and performance characteristics are directly related to cross-linker levels. Low concentrations of cross-linking agent yield coatings which are soft, water sensitive, and do not resist detergent solutions and the weather. Elevated levels of curing agent have equally undesirable effects since coatings become brittle and lack sufficient adhesion to the substrate. In addition to cross-linking agent, nitrogen content provides information on the presence of polyamide and urethane polymers, which also contain nitrogen.

Vehicle Identification

Infrared Spectroscopy

Qualitative infrared spectroscopy is a valuable analytical tool which allows the examination of the multitude of materials utilized in the coatings industry. It is the primary tool for vehicle/resin identification in a coating. An infrared spectrum indicates the overall composition of any unknown material in terms of its functional groups. With a minimum of background knowledge, substantial information can be gained from an infrared spectrum by simple functional group identification. However, beginners should be cautioned against making unfounded conclusions based strictly on this technique. As one becomes more acquainted with infrared spectroscopy, the limitations and real complexity of this analytical technique will become more apparent. All laboratories involved in the infrared analysis of any aspect of coatings should have available a copy of "An Infrared Spectroscopy Atlas for the Coatings Industry" published by the Federation of Societies for Coatings Technology [4]. This atlas (inclusive of a 2500-spectra library) is an invaluable tool and a true benefit to the spectroscopist in the coatings industry.

Occasionally, it is possible to obtain some qualitative information from the infrared spectrum of a pigmented binder system if the system is relatively simple. However, a binder free from pigment should be obtained for an infrared analysis. This means prior separation of pigment, vehicle, and solvent and a further breakdown of these fractions if possible. The elemental composition of the fraction should be obtained because in some cases the presence of certain elements will not be obvious from the infrared spectrum [4].

In most cases, band positions are indicative of the functional groups present. The shape of the bands also gives information concerning the functionality of a molecule. The relative intensity of a band in comparison to the intensity of other bands provides information pertaining to the amount and identity of a specific functional group present in a molecule. Functional groups that give rise to a large change in the dipole moment of a molecule, upon undergoing a vibration, will have very intense absorption bands. Excellent examples of this phenomenon are the carbonyl and ether groups [4].

Once it is known which bands are characteristic of certain functional groups, the absence of these bands from a spectrum can be used to establish which functional groups are not present in detectable amounts. This method of analysis is important since the spectroscopist is frequently requested to establish the presence or absence of a particular functionality. If there is absorption present in a particular region, no information can be obtained from that region by negative interpretation. Positive interpretation or other techniques must then be relied upon [4].

The simplest method of interpretation is to consider the entire spectrum as though it were a picture and compare this picture with the spectrum of known materials which have been physically or mentally cataloged. If the spectra are the same, or very similar, it is a reasonable assumption that the materials are nearly identical. As experience is gained and more spectra are committed to memory, a great many materials can be recognized by inspection. Reference spectra prove invaluable in this type of interpretation, especially when a definite identification must be made [4]. There are also very extensive collections of reference spectra with which one tries to match "fingerprints" of unknown materials in order to make positive identifications.

In most cases, the limit of detectability of one material in another by infrared spectroscopy is 5%. However, depending on the type of material, it may be less than 1% or as high as 30%. The limit of detection will depend on the phase, the absorptivity of the particular absorption being used, and the proximity of this band to other strong absorptions. Therefore,

it is important to rely upon previous knowledge of the system and to use other confirmatory methods to verify the infrared analysis [4].

In addition to determining polymer type and concentration, the detection of contaminants in complex matrices and the examination of residual reactive functional groups can be done by infrared. The technique has advantages over other analytical techniques in that literally any type of sample can be examined by IR: solids, liquids, or gases. Special techniques are also available to examine surfaces.

Extension of a UV-VIS experiment into the near-infrared region allows examination of materials which absorb in that region. Wavelengths in the near-IR region are those longer than visible wavelengths and occur below the red portion of the visible spectrum. A special source and detector are needed to extend into the near-IR, but instrumentation is available which will automatically switch to these at the proper wavelength. A special technique is utilized in the near-IR called diffuse reflectance and is used to measure the total reflected light off of a painted surface. This is done with a device called an integrating sphere which collects all of the reflected light from a surface and focuses it to the detector. In this way, one not only measures the amount of light a sample will absorb, but how much is reflected as well.

Infrared has great utility for the quantitative analysis of polymers, inorganic pigments, solvents, and additives. Solubility of the sample is not a requirement, and many complex mixtures can be determined in this fashion. With the increased utilization of Fourier Transform and computer-assisted dispersive infrared spectroscopic techniques, quantitative applications have been further enhanced. The basis for quantitative analysis is, of course, the Beer-Lambert Law [4].

Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance spectroscopy permits the qualitative and quantitative analysis of many organic materials. When certain nuclei are placed in a strong magnetic field, their nuclear spin states are split into two or more levels due to the magnetic properties of these species. Transitions between these magnetically induced energy levels can then be brought about by the absorption of radio frequency energy. The specific frequencies of the radiation subsequently re-emitted depend on both the chemical and magnetic environment of each nucleus, such that detailed structural information is possible. NMR, as an analytical technique, provides information about how the atoms in a molecule are arranged. It is possible to determine which carbons are present as methyl groups, methylene groups, and so forth. The number of hydrogen atoms attached to oxygen and nitrogen can also be determined, and with these pieces of information the analyst is able to generate a molecular structure.

Samples that are soluble in a variety of solvents can be examined using nuclear magnetic resonance spectroscopy. It is ideal for structural identification of organic compounds. Qualitative and quantitative analysis of polymer composition, quantitative measurement of polymer mixtures, analysis of copolymer sequence distribution and tacticity, analysis of type and degree of polymer branching, and polymer end group analysis can all be done with NMR. An NMR spectrum of a typical polyester would show each of the dibasic acids and the polyols used in the synthesis of the polyester. NMR can be a superb asset to the analyst along with other tools such as IR for identification of true unknowns and for assisting polymer synthesis identification work.

Miscellaneous Testing

A host of chemical methods exist for further identification of resin components by chemical treatment of the resin to break it down into its original starting components, which can then be analyzed by conventional methods. For example, a resin may be subjected to aminolysis to form amides of the carboxylic acids and to release the polyols. Upon further treatment, these materials can be readily identified. Scanning of available ASTM methods and Official Methods of Analysis of the Association of Official Analytical Chemists (AOAC Methods) [7] will provide insight into other useful techniques and procedures.

Thermal analytical data can also aid in the identification and characterization of a polymer. DTA or DSC can be used to obtain a melting point, a T_g, and a measure of the thermal stability of the polymer. XRD analysis of the polymer will determine if the polymer is partially crystalline, help to identify the chemical structure of the polymer, and provide information on the preferred conformation of the polymer chains in the crystalline regions [6].

Electron microscopy and XRD techniques describe the submicron morphological features of polymers such as lamellae and crystallites, while optical microscopy is used to study large morphological features such as the size and nature of spherulites in a polymer [6].

Electron probe microanalysis (EPMA) is an elemental identification technique associated with SEM. When materials are bombarded by a high-energy (10 to 50 keV) electron beam, characteristic X-ray fluorescence radiation is produced. By incorporating either energy dispersive or wavelength dispersive spectrometers directly into the instrument, it is possible to obtain X-ray spectra directly on the area as seen by the electron beam. Thus, it is possible to obtain qualitative and quantitative elemental data from a small volume of material for the elements boron through uranium. EPMA has been used extensively for impurity and inclusion identification in polymers [6].

Some unique vehicles may be particularly difficult to analyze, and the determination of residual monomer by gas chromatography often can shed some light on the resin system.

Pigment Identification

The following sections discuss the qualitative and quantitative identification of pigments.

Infrared Spectroscopy

As noted in the discussion on vehicle identification, IR analysis for the qualitative identification of pigments is most common. Procedures and reference spectra may be found in the Infrared Atlas [4]. Infrared is also used for identification of extender pigments.

Inductively Coupled Argon Plasma Spectroscopy

Inductively coupled argon plasma spectroscopy, often referred to as ICP or ICAP, is a technique used to determine the concentration of various elements present in any sample or

material. The instrument can provide qualitative and quantitative information and can complete an analysis on numerous elements simultaneously and in a matter of a few minutes. The major strength of the technique, aside from speed, is the ability to detect trace amounts of elements.

A solution is aspirated into the instrument, where a fine aerosol is formed. This aerosol is then introduced into a high-energy argon plasma, where the elements present in the sample are raised to an excited state. When these elements return to ground state, they emit light at wavelengths characteristic of the elements present. The intensity of the light is proportional to the concentration of the element present in the sample. Generally, sensitivity is in the low parts-per-million range for most elements.

The plasma is a highly ionized, chemically inert, hot gas which achieves a temperature estimated to be 10 000°C. A radio frequency generator provides energy to the plasma torch by creating an oscillating magnetic field. A sample introduction device, known as the nebulizer, converts the sample solution into fine droplets or aerosol mists which are transported to the torch by means of argon carrier gas. The high temperature of the plasma dries the droplets and decomposes the sample into individual atoms which are excited and emit light as they return to the ground state. The wavelength of the light produced differentiates one element from another. The intensity of the light produced is a measure of the concentration of the element present in the sample.

The light emitted from a sample containing many elements passes through an optical path which separates the spectrum of light into discrete wavelengths. A detection system, made from many photomultiplier tubes, each representing a wavelength of an element, measures the intensity of light and converts it to electrical energy. The electrical energy is converted into concentration by means of a dedicated computer. The computer performs all instrumental control functions and prints the data.

Some applications of ICP are the following: pigment composition in coatings, industrial influent and effluent analysis, soluble cations and anions in electrocoat baths, organo-metallic additives in coatings, driers and catalysts in coatings, competitive product analysis, quality control of raw materials, and industrial hygiene analysis.

Atomic Absorption Spectroscopy

Atomic absorption spectroscopy, commonly referred to as AA, is designed for measuring the concentration of metallic elements in solution at the parts-per-million level. Atomic absorption is an efficient and sensitive method for performing routine quantitative analysis with a high degree of precision and accuracy. Unlike inductively coupled plasma (ICP) spectroscopy, this instrument is only capable of analyzing the concentration of one element at a time. Thus, it is more often recognized for its quantitative power rather than its qualitative capabilities.

Atomic absorption methods rely on the absorption of light by atoms. If a solution containing metal ions is aspirated into a heat energy source, such as a flame, the high temperature and environment of the flame causes the formation of free, ground-state atoms in the flame. These free atoms are capable of absorbing light of a particular frequency. If a beam of light having the appropriate frequency or energy passes through the flame, the free atoms in the flame will absorb some of this energy. The decrease in the intensity of the light beam can then be taken as a measure of the concentration of that particular element in the sample solution.

Atomic absorption instrumentation requires a light source, an atomizer, a monochromator, and a detector. The normal light source used in AA is a hollow cathode lamp. It consists of a hollow cup made from the element to be analyzed. Application of a high potential causes formation of positively charged ions which bombard the cathode, forming excited metal ions which emit light. AA is important since free, uncombined atoms must be formed before light absorption occurs. A solution containing the metal ions is heated to a temperature sufficient to dissociate the ions into atoms. The heat energy can be provided using an air-acetylene or nitrous oxide-acetylene flame. The primary function of the monochromator is to isolate a single atomic resonance line from the spectrum of lines emitted by the light source and direct it through the flame and onto the detector. Photomultiplier tubes are employed as detectors. They measure the changes in light intensity and convert them to electrical signals.

Sample preparation is an essential part of AA. Solid and pigmented samples are ashed to remove organic species. The inorganic components are dissolved in acid and diluted with deionized water prior to introduction into the flame. Nonaqueous AA is an ideal way of determining organometallic compounds to prevent sample loss or conversion of the metallic species into insoluble components.

Atomic absorption complements ICP techniques for the analysis of paints, resins, UV curable coatings, and other materials. It is also a very useful tool in analyzing waste materials, pigment composition, pollution studies, raw material evaluation, and analysis of organometallic compounds.

Several pigment analysis procedures using AA are standard ASTM methods. Typical procedural examples of AA analysis for pigments can be found in the following:

Standard Test Method for the Determination by Atomic Absorption Spectroscopy of Titanium Dioxide Content of Pigments Recovered from Whole Paint (D 4563)

Test Method for Detection of Lead in Paint by Direct Aspiration Atomic Absorption Spectroscopy (D 4834)

X-Ray Fluorescence Spectroscopy

X-ray fluorescence (XRF) is a relatively simple and, in general, nondestructive method for the analytical determination (qualitative and quantitative) of elements. This method is extremely useful because of the ease of sample preparation and its ability to "scan" the periodic table for all elements down to aluminum and sometimes boron. The technique allows for rapid qualitative determination of the elements present. ASTM Test Method for Determination by X-Ray Fluorescence Spectroscopy of Titanium Dioxide Content in Paint (D 4764) is a typical application for the technique.

X-Ray Diffraction

The X-ray diffraction (XRD) pattern obtained from a material is characteristic of that material. The intensity of a diffraction peak is entirely due to one component of a mixture and is dependent upon the amount of that substance in the mixture. To a minor extent the peak intensity of the component is also dependent on the mass absorption coefficient of

other materials present. Since the method utilizes the ratio of diffraction maxima of two chemically similar materials, it is expected that the effects of other constituents will be the same for both materials.

Diffraction measurements can be made on single pigments, pigment mixtures, on films of pigmented coatings and on films prepared from liquid coatings if interfering materials are not present. ASTM Test Method for Ratio of Anatase to Rutile in Titanium Dioxide Pigments by X-Ray Diffraction (D 3720) is an application well suited to this technique.

Chemical Methods

The typical chemical methods using titrimetry and gravimetric procedures are always appropriate for quantitative pigment determinations. Some of these techniques have been replaced in recent years by more efficient (not necessarily more accurate) and time saving instrumental methods; however, there are situations where the traditional testing methods are still most appropriate.

Numerous ASTM methods exist for these types of analysis, and one needs to check the index of available test methods. By way of example, the following are noted:

ASTM Test Methods for Chemical Analysis of White Titanium Pigments (D 1394)

ASTM Test Method for Arsenic in Paint (D 2348)

Additive Identification

Additives can often be the most difficult components to analyze and identify in a coating. They frequently are present in small quantities (often at a few percent or less), and their presence can be masked by major components. In addition, the number of possible additives is large and includes surfactants, plasticizers, defoamers, thickeners, anti-oxidants, etc. It takes a skilled and experienced coatings analyst plus good deductive problem-solving ability to become adept at additive analysis. The volatile nature of some co-solvents, coalescing agents, and some plasticizers makes their identification by gas chromatography fairly straightforward.

Infrared Spectroscopy

For samples containing mixtures, the IR spectrum generally gives information only about the major component(s). However, computerized infrared instrumentation allows one to subtract spectra of the major constituents from a mixture and get the resultant spectrum of minor materials such as additives and contaminants. Thus, it is possible to do a spectral "separation" in just a few seconds rather than a true chemical separation which may take hours. Water and hexane extractions of dried films followed by IR can point to some of the following, for example:

- Cellulosic thickener (which can be confirmed by spot test).
- Long chain aliphatic hydrocarbon "oil" is indicative of defoamers.
- Carboxylate containing component may indicate a polyacrylate salt.
- Nitrile component may indicate mildewcide.
- Di-alkyl sodium sulfosuccinate is indicative of a wetting agent
- Inorganic sulfate may be a possible persulfate polymerization catalyst.

High Performance Liquid Chromatography

High Performance Liquid Chromatography is frequently referred to as HPLC or just often as LC. This technique is used to separate components from mixtures, especially nonvolatile components which are not amenable to GC analysis. Since these nonvolatile components represent about 90% of all organic compounds, HPLC separation techniques offer extraordinary versatility and capability. Components may be separated either by size or subtle differences in molecular configuration and solubility. Separations based on size are commonly called gel permeation chromatography (GPC) or size exclusion chromatography (SEC). Separations based on subtle differences in molecular configurations and solubility are called partition chromatography. Both quantitative and qualitative information can be obtained by using HPLC techniques.

Samples to be analyzed by HPLC are dissolved using an appropriate solvent or a combination of solvents before they are introduced into the liquid chromatograph. Samples which are not soluble in HPLC solvent(s) are not suitable for analysis using this technique. The actual separation process takes place on a packed column or a series of packed columns through which solvent is constantly pumped. The separated components elute from the column(s) directly into a detector. The detector is connected to a recording device which produces a trace of the separated components versus time, i.e., a chromatogram.

The two most common detectors in HPLC are the differential refractometer and the ultraviolet (UV) spectrometer. The refractometer measures the difference in refractive index of the solvent and the component being analyzed. The ultraviolet spectrometer measures a compound's absorbance at various wavelengths in the ultraviolet (or sometimes visible) region of the light spectrum. The refractive index detector is most commonly used with size separations, while the ultraviolet detector is usually used in conjunction with partition chromatography. The ultraviolet detector is capable of detecting components in the part-per-million (ppm) range. The refractive index detector, on the other hand, can only detect components down to the 2 to 4% range. It is referred to as a universal detector because it is not dependent on the sample components absorbing at a particular wavelength of light.

Typical applications include: surfactant evaluation, polymer characterization, additives in polymers, air and water pollution, raw material evaluation, multi-functional acrylates, plasticizers, coalescents, and cross-linking agents.

Ultraviolet and Visible Spectroscopy

Ultraviolet and visible spectroscopy (UV-VIS) examines the absorption of UV and visible wavelengths of light by a sample. This type of analysis is often used as a quantitative measure of a material. Materials which possess aromatic rings such as polystyrene, alkyd resins, and many paint additives will absorb UV light and can be examined. Materials which absorb in the visible region of the spectrum are those which possess color. Chemicals such as dyes can be examined in that region. UV-VIS is very sensitive for the species that absorb in these regions, and concentrations in the low parts-per-million range can usually be determined.

The visible region of the spectrum consists of wavelengths seen through the eye. In a visible instrument, a tungsten

filament light is used as a source of visible wavelengths. Wavelengths are separated by a grating and examined one at a time. A photocell detector is used to measure absorbance at each wavelength and a spectrum is recorded.

Ultraviolet wavelengths are shorter than visible wavelengths and occupy the region above the blue end of the visible spectrum. To observe ultraviolet absorbencies, a mercury lamp is used as a source of UV light. Wavelengths are separated by a grating and detected, again by a photocell. An ultraviolet spectrum looks similar to a visible spectrum. Modern instruments combine UV and visible detection, and as the spectrum is being scanned the instrument will automatically switch from one source to another. Observed absorbencies are directly proportional to concentration of the component of interest.

Materials which do not absorb in the UV or visible region can sometimes be measured by complexing them with an absorbing reagent, usually to develop a colored species. Very sensitive methods of this type are used for the determination of formaldehyde, phosphorous, and sulfate.

Solvent Identification

Gas Chromatography

Gas Chromatography (GC) is a technique for the separation of any species exhibiting a measurable vapor pressure at a temperature up to approximately 300°C, as well as any compounds for which a stable, volatile derivative may be formed. Both qualitative and quantitative information can be obtained.

Most GC samples are liquids or solutions at room temperature, although instrumentation may be adapted to analyze solid and gaseous samples. Liquid samples (approximately 0.001 mL) are introduced to the instrument using a syringe into a flash heating chamber called an injection port. There, the volatile sample components are quickly and evenly vaporized. In some cases, however, decomposition of sensitive components can occur when they come in contact with the hot metal surface. The analytical chemist may be able to minimize or circumvent this problem if proper precautions are taken. The vaporized components are then carried onto the column and through the gas chromatographic system using an inert gas, such as helium or nitrogen, flowing at a constant rate.

The column is the portion of the chromatograph where the actual separation of components is achieved. A packed column consists of narrow tubing made from stainless steel, nickel alloy, glass, or a number of other materials, filled with fine particles of a packing material. This packing material may consist of polymeric beads or an inert solid material supporting a thin film of a non-volatile liquid. It is the varying degree of interaction between each of the sample components with the packing material that causes the components to become separated in the column. A large number of packing materials of varying chemical composition are available. Columns containing other packing materials are easily interchanged so that different separations can be obtained.

Occasionally, samples will contain a number of components of similar volatility and/or chemical composition which are difficult to separate on packed columns. In these instances, capillary columns are used. Capillary columns are extremely long (100 to 300 ft, 30.48 to 91.44 m), narrow bore tubes made from glass, metals, or fused silica. They are internally coated with a thin film of a nonvolatile liquid to effect separation. A variety of detectors used alone or in combination can be strategically mounted at the end of the column to monitor the separated components as they exit the column. The detectors available in GC have varying sensitivity and specificity. If needed, some may be operated to detect materials in the sub parts-per-million level.

The response of the detector to an eluting component is electronically converted into a visual representation called a chromatogram. A chromatogram is a plot of detector response versus time elapsed since sample injection. Eluting components are represented as peaks in the chromatogram. The time needed for a component (peak) to elute can be used to help identify the component. The area produced under the peak is related to the concentration and is used in the quantitative determination of the component.

Typical applications include: qualitative and quantitative solvent analysis, odor analysis, pollution studies, purity determinations, determinations of residual monomers, and determination of airborne organic contaminants.

Additional information on gas chromatography may be obtained from ASTM Practice for Packed Column Gas Chromatography (E 260). ASTM Test Method for Direct Injection of Solvent- Reducible Paints into a Gas Chromatograph for Solvent Analysis (D 3271) describes the techniques used in many situations. Note should also be made of ASTM Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph (D 4457) for exempt solvent analysis for VOC calculation purposes. ASTM Committee E19 on Chromatography is focused on chromatographic techniques. There are numerous ASTM gas chromatographic test methods for the determination of the purity of specific solvents and for the determination of specific impurities such as benzene.

Gas Chromatography—Mass Spectrometry

Gas chromatography has been well established as an excellent tool for the separation of volatile species in complex mixtures. A significant limitation of gas chromatography, however, is the relative inefficiency and lack of certainty in this technique when the identification of unknown components is required. Mass spectrometry is an excellent tool for qualitative analysis. However, if a complex mixture is introduced into the instrument, the resulting mass spectra of all components are superimposed on one another, making analysis difficult, if not impossible. These limitations are overcome by a combination of gas chromatography and mass spectrometry. Sample constituents are separated into pure components using the gas chromatograph; these pure components are then introduced into the ion source of the mass spectrometer for identification. Generally, samples are liquids; however, gases and solids can also be examined.

As the sample components enter the mass spectrometer, they are immediately ionized. Electrons are removed from the sample molecules resulting in the formation of positively charged ions. This is normally accomplished through electron impact or chemical ionization. Each of these ionization

techniques has unique properties for providing useful analytical information.

Electron impact ionization occurs when electrons emitted from a hot filament collide with sample molecules causing the loss of one or more electrons. This results in the formation of positive ions which contain excess energy. The excess energy causes many of the resulting ions to break apart or fragment, thus providing the fragmentation patterns used to determine chemical structure.

In chemical ionization, the mass spectrometer's ionization source is pressurized with a reagent gas such as methane, ammonia, or butane. Electrons from the filament collide with, and impart energy to, the reagent gas. The energetic reagent gas molecules subsequently collide with the sample molecules causing the sample molecules to become positively charged. Ions formed in this manner do not contain as much excess energy as ions formed via electron impact ionization. Consequently, very little fragmentation occurs and intact ions containing molecular weight information are obtained.

Following ionization, the sample and fragment ions are sorted according to their respective masses. Ion intensities at each mass are measured by an appropriate detector, and the corresponding signals are transmitted to a computer for further processing and data storage. Results can then be displayed in graphical or tabular form. Interpretation of the spectra and comparison with a library containing thousands of reference compounds allows sample composition to be determined by the analyst.

Typical problems examined using GC-MS include: the qualitative identification of volatile organic species and contaminants in coatings and coatings raw materials, quantitative analysis of volatiles at the parts-per-million and parts-per-billion level, evaluation of potential odor causing species, and determination of polymer composition following pyrolysis and chemical degradation. Other uses include: characterization of complex solvent systems; monitoring of waste streams and ground waters; characterization of polymer products, by-products, and intermediates; identification of odor problems; and monitoring of raw materials for potential contamination.

TRACE ANALYSIS

With the development of sophisticated instrumentation over the past two decades, the ability to increase sensitivity in lower detection limits for many materials has increased. This is particularly true in the areas of metals analysis. As a result, many regulatory and compliance agencies have changed their detection limits to reflect this increased capability. For EPA (Environmental Protection Agency), OSHA (Occupational Safety and Health Administration), and FDA (Food and Drug Administration) compliance, trace analysis is extremely important. Many manufacturers require trace analysis to identify contamination, to verify product purity, and so forth. Analysts must be prepared to provide data in the parts per billion (ppb) and sub ppb range when necessary, and this frequently involves good concentration techniques as well as good methodology and instrumentation.

Certainly techniques such as GC, MS, and HPLC are capable of measuring components in solution well below the ppm range. The specificity of mass spectrometry and its sensitivity for organic compounds has made it a common tool used in EPA protocols for pollutant-related analysis. Coupled techniques such as GC-MS, LS-MS, and ICAP-MS are also available today and can provide very low-level analysis. Commonly used trace element procedures such as AA, ICAP, ion selective electrode analysis, neutron activation analysis, and optical emission spectroscopy all offer low-level analysis. ICP-MS detection capabilities are comparable to those of graphite furnace atomic absorption spectrometry. For many elements ICP-MS provides quantitative analyses down to the parts per trillion level.

In addition, for inorganic compounds, scanning electron, microprobe, and transmission electron microscopy are useful for trace analysis. Surface techniques such as X-ray photoelectron, Auger, and SIMS are also useful as qualitative and quantitative measurement techniques.

At the very small concentrations that characterize trace and ultratrace analysis, and with the minute samples employed in microanalysis, the limit of detection, a new criterion of performance, becomes important. Because noise itself now becomes limiting, many questions arise. For example, how large must the reading from a sample be compared with that from a blank for a person to report that analyte is present?

At the detection limit, statistics and chemistry become intimately mixed and statistical procedures must be used to interpret chemical results. The detection limit is simply the smallest concentration of analyte that can be certified as statistically different from a blank. To determine the limit, two sets of measurements are necessary. In addition to a regular set, many measurements (10 to 20 are recommended) must be made on a blank under the same conditions. It must simulate regular samples but be without analyte.

To calculate the limit of detection, one begins by observing the limiting response. For a given measurement procedure, it is the smallest response that can indicate with reasonable probability that a particular analyte is present. To obtain the limit of detection from the limiting response requires a calibration curve or a standard addition curve. A usable curve will be one based on quite pure standard solutions of extremely low concentration. The alternative, a long extrapolation of a calibration curve beyond the lowest points for standards even in those favorable cases in which the curve is linear, will invite substantial error.

Actually, as quantitative measurements at the trace level have become more important than simple detection, a limit of quantification or *limit of determination* is recommended by IUPAC for comparison of the relative merits of different trace methods rather than the limit of detection.

The future of analysis will become more sophisticated with the development of more sensitive instrumentation and computer technology. Robotics and autosampling will also enhance the development of analysis and reduce the amount of error that is introduced in analysis. These changes tend to impose more sophisticated demands in analysis from customers and regulatory agencies. There is a tremendous burden on the analyst to be conscious of extraordinarily good laboratory techniques, the limitations of the instrumentation, and the reporting of sound data.

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The Analysis of Coatings Failures

by George D. Mills[1]

THE TESTING OF COATINGS always has a relationship to coating failures, either directly or indirectly. Testing before failure helps to ascertain serviceability, establish the best formulation variables, maintain quality assurance of coating products during manufacture, develop storage and application parameters, ensure specification viability, and, in essence, prevent early failure. Testing after failure assists in determining cause, hopefully prevents future coating failures of a similar nature, and aids in placing liability.

Failure modes run the full gamut. Coating failure can originate from within, as with deficiencies in a coating's formulation or its manufacturer. Anomalies in the coating's film-forming chemistry from competing atmospheric side reactions are very common with some urethanes and epoxides. Failures can originate external to the coating material from improper specification, inappropriate or inadequate surface preparation, and application deficiencies.

The analysis of coating failures should follow a systematic program based on the "scientific method." Briefly this translates to: (1) investigate; (2) hypothesize; (3) test; and (4) conclude or reconsider. Test programs after failure are often a part of the failure analysis process and have the purpose of establishing viability of a proposed failure mechanism. Designing the test and evaluation program requires a knowledge of the total process from specification to paint manufacturing to paint application. In part, it requires a knowledge of the laws of physics and chemistry that are controlling what is happening at interfaces. The coating system contains many types of interfaces including the substrate/coating interface, emulsion resin particle/carrier surfaces, intercoat interfaces, and the interfaces between the pigments and binder in the coating formulation. The chemistry and physics of solutions controls apparent viscosity and can impact osmotic failure modes. Polymer curing and weathering reactions, corrosion, and dimensional stability are just a few of the other sources of coating failures often reported. As a preliminary to designing test programs to determine failure modes, the investigator must appreciate not only the processes of surface preparations, cleaning, and pretreatments, but coating application techniques as well. He must be knowledgeable about the different types of coatings and their typical degradation and stabilization mechanisms.

Coating failures may manifest themselves as a change in physical or chemical properties. Changes in gloss, color, extensibility, chemical resistance, and vapor/gas transmission coefficients are common problems. Failures associated with delamination of a coating from its substrate are usually classed as "adhesion" failures, although they are often a delamination through a weak boundary layer (WBL) near the interface. Osmotic activity from solvents or coating constituents within the film and salts beneath are common failure modes in some environments. Underfilm corrosion is often considered as a coating failure and may result in substrate damage.

Coating failure analysis is extremely important for various reasons. The most important is simply to "ensure" that the failure doesn't happen again. While this sounds noble, the experience of most investigators is to the contrary, for one sees the same problems occur repeatedly. Paints and coatings are very sophisticated chemical systems. Since all of the natural forces impacting the chemistry and physics of the system are operative, the total picture is seldom known. Most often, a very naive conception of the situation is developed and action is taken for one particular reason while failing to consider a multitude of other less familiar causations.

Truly successful investigations of coating failures necessitate knowledge of the coating system's chemistry and the many applicable evaluation and test procedures available. To appreciate which test regime would be appropriate for a specific failure situation, the investigator must understand much about the coating itself. This includes knowledge of the components of the coating, its curing chemistry, the chemistry and physics of its interfaces, and any interfering and competing atmospheric side reactions. Application equipment and procedures, with a host of related potential problems such as off-ratio mixing, use of thinners that are nonsolvents or contaminated with water from storage outside, as well as potential paint manufacturing problems are additional typical sources of coating failure problems.

Designing the proper test regime before a coating failure occurs is very important. It is difficult, if not impossible, to assess all of the variables that will be seen in the field after the coating is applied. Reconstruction of a failure situation is even more difficult, and it is usually impossible to match the original application situation totally. This is particularly true in off-ratio mixing problems. Advanced instrumental techniques using cryotrapping of pyrolized polymer fragments followed by gas chromatography using a mass spectrometer as a detector have proven extremely helpful [*1*].

The design of a test program to demonstrate feasibility of a particular failure mode is best accomplished by considering five basic questions. These questions guide the investigator

[1]President, George Mills and Associates International, Inc., P.O. Box 847, Humble, TX 77347.

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through the logic that aides one in understanding the potential failure modes. These questions are as follows:

1. What is the actual coating failure?
2. What is the coating system?
3. What was the desired purpose of the coating?
4. How was the coating applied?
5. What evidence is presented by the failure?

WHAT IS THE ACTUAL COATING FAILURE?

A coating failure exists when a coating fails to accomplish all of its intended tasks during its engineered design life (EDL). Usually, a failure in a particular primary property prompts the investigation. The first step in analyzing a failure is to clearly define the problem. While this appears at first glance to be an easy and straightforward task, it is not. A typical example is the mistake of identifying a delaminated coating automatically as lost adhesion. Adhesion, by definition, is between two dissimilar surfaces. In contrast, cohesion is between two of the same surfaces. There can be numerous reasons for a coating to break away from its substrate. While adhesive loss is possible, cohesive delamination within a weak boundary layer is very common. A good example is a coating applied over improperly prepared zinc galvanizing where cohesive failure occurs in the zinc oxide-zinc carbonate layer and is automatically written off as a saponification problem, even though the coating may not be susceptible to (or capable of) saponification. Another very common cohesive failure is the apparent delamination of an amine-cured epoxy applied over an amine carbonate that has formed on (or exuded from) an earlier applied epoxy coating. This cannot usually be seen with the unaided eye. Splitting within a "transparent" layer near the interface will appear as if the problem is adhesive rather than cohesive failure. Interrogation of the coating interfaces by the proper instrumental technique is the only way to determine the locus of failure.

Many tests associated with coatings may be brought to bear in providing answers. While most of these tests are established ASTM procedures, some are related to task-specific, chemical analysis. These include auger spectroscopy, X-ray photoelectron spectroscopy (XPS), and other surface analysis techniques that are limited to "seeing" only the outer few angstroms of the surface. Ion bombardment, which ablates the surface, allows "seeing" an elemental analysis as a function of depth into the outer layer. Techniques such as energy dispersive X-ray (EDX) will evaluate the surface but are much more energetic, thus giving an average elemental analysis much deeper into the sample being evaluated [*7*].

Osmotic blister formation is another area often misunderstood. Osmosis requires one solvent (by definition, the specie present in the greatest concentration) and one or more solutes. Analysis of the blister fluid is required to determine the source of the driving force. While water is often the source of solvent with inorganic salts or organic solutes, other organic products are seen as the norm in some industrial tank-lining problems. Analysis of the blister fluid is best accomplished by GC/MS for organic solutes [*1*] and ion chromatography or EDX (after evaporation) for inorganic solutes [*7*]. To the contrary, "blister-like" formations in inorganic zinc-rich or flame-sprayed metallic coatings may look like osmotic blisters, but they are usually caused by the production of powdered corrosion products under or within the film [*2*]. It is safe to say that the problem cannot be solved and proper liability placed until the true coating failure problem has been identified.

WHAT IS THE COATING SYSTEM?

Failures are often related to the generic type of coating under investigation. As such, the failed coating should be identified as a preliminary step in understanding the potential failure modes that exist leading to the failure. Alkyds have failure modes different from acrylic latex systems. Epoxides will often fail differently from urethanes. Alkyds over vinyl primers are susceptible to water vapor transmission problems. Moisture-cured systems such as urethanes, epoxies, and ethyl silicate zinc-rich systems when applied in very dry atmospheres cannot cure properly. Urethanes and some latex systems present problems in wet atmospheres.

Although a coating is any material applied to another surface, each coatings practitioner will have a view of coating systems shaped by his/her experiences. While most coatings are paint-like in nature, many have strikingly different appearances and characteristics with correspondingly different failure modes and different required test regimes. The coatings manager at an automobile factory might work with inorganic metal pretreatments, electro-deposited primers, and robotically applied color coats with wet-on-wet UV-resistant clear topcoats followed by water-repellant surface modifications. The pipe corrosion specialists will encounter conventional liquid paints, fused powders, flame/arc-sprayed metallic powders such as zinc, aluminum, or high alloys, and plastic tapes wrapped around the pipe with or without primers for external protection. Internal pipe coatings may be the conventional liquid and powdered coatings as well as thin cement linings like those found in many potable water supply lines or fused polyethylene mixtures. Because of this great diversity, the coatings analyst will address coating failures of many generic types of films including organic, inorganic, and metallic.

Paints form the largest subgroup of coatings and, as such, will be the focus of this section. Analyzing coating systems before and after failure requires many different testing procedures. Many of these standardized procedures can be found in Volume 6.01 through 6.04 of the *Annual Book of ASTM Standards* [*3*]. To be efficient, the investigator must have knowledge of the paint formulations of many generic types. Knowledge of the polymer's typical failure mechanisms, individual polymer chemistries with their respective degradation mechanisms, and typical stabilization methods are also very helpful [*4*]. An efficient investigation requires an appreciation of the tools and instrumentation that can be brought to bear and is tremendously important in determining the testing regime best suited to a particular type of failure problem. This includes knowledge of the capabilities and limitations of the analytical instruments being used as well as the ability to interpret and challenge test data when necessary.

Typically, a paint may be considered as being composed of four "subsystems," any one of which may produce a coating failure. These are: (1) the resin or binder system; (2) the

pigment system; (3) the solvent or carrier system; and (4) the additives package. The resin or binder system holds the pigments together and provides physical characteristics such as electrical resistance, flexibility, water and gas permeability resistance, adhesion, etc. The pigment system serves to provide coating strength, vapor transmission resistance, anticorrosive properties at a metal interface, abrasion resistance, and other film property enhancements. For less than 100% solids systems, the carrier system is usually a solvent or dispersing media. For 100% solids liquid coatings, the dispersing media may be air or the pressure from an airless application system. For powder coatings, super dry air is the delivery system, transporting the fluidized powder through the delivery lines. The additive package is meant to produce specific effects to the coating system when included in low concentrations. Additives may address potential problems with the preapplied paint "in the can" or address potential film problems after application. Coating failures may originate from problems associated with quality control of the paint's manufacture as well as problems associated with long-term storage or application. Each type of coating will have some characteristic failure modes, although certain modes will be common to all.

Failure Modes Associated with a Generic Type of Coating

Failure modes tend to follow generic types of coatings. In a very broad sense, coatings may be grouped into three categories based on the final film. These are coatings with organic binders, those with inorganic binders, and those composed of metallic films. The largest category of coatings are those utilizing an organic binder. Organic binders use polymers based on carbon as the primary atomic makeup of their backbone. The paint film at application includes polymer precursors using functional groups such as epoxies, urethanes, vinyls, acrylics, and alkyds. These must polymerize to reach some high molecular weight at which they are capable of forming protective films. Generally, inorganic coatings are those that utilize elements other than carbon for forming a film. These may be silicates, sulfates, or cementitious coatings based on calcium. As a coating, each will have some typical failure modes. Metallics may be very thin films used on plastics for affecting gas molecule transmission and abrasion characteristics. They may be thick as from galvanizing or flame/arc-sprayed metallics used for corrosion protection.

Organic Resin Binders: Polymers Based on Carbon

Paints and coatings using organic binders are by far the largest category and will provide the greatest challenge to the failure analysis investigator. These will include binders derived from vegetable oils, petroleum, and cellulose. They can be separated further into groups based on their curing functionality or their polymer origination such as epoxies, urethanes, alkyds, acrylics, or vinyls. They may also be classed by their dispersion system such as solvent, emulsion, powder, waterborne, or 100% solids.

Organic resin binders will utilize some mechanism for producing the protective film. This film forming/curing mechanism is a potential source of failures. A failure may manifest itself as a film with poor flexibility, weatherability, chemical resistance, adhesion deficiency, or a host of other shortcomings.

The formation of a paint film may come about by various mechanisms, each having distinctive failure modes. Some typical examples include: (1) lacquers; (2) oxidative binders requiring oxygen from the atmosphere; (3) moisture-cured binders; (4) chemically reactive cross-linking binders; (5) heat-activated binders; and (6) nonthermal, high-energy cured binders.

Lacquers are coatings containing polymers dissolved in a suitable solvent system that evaporates to yield a film. While these coatings are called "lacquers" in the United States, in Europe and other parts of the world, the word "lacquer" is often used interchangeably with the word "paint." Film testing may address sanding characteristics, abrasion resistance, drying times, gas or water vapor permeability, gloss, and color retention, among other film properties. With essentially no chemical cross-linking occurring, the solids deposited on each coat will be determined by the maximum lacquer viscosity that allows application. Since this is related to the polymer's average molecular weight, which must be high for toughness and strength, films of low dry film thickness (DFT) are often seen, and the applied solids will be low. Lacquer film properties are strongly impacted by the solvent system, humidity and other ambient conditions, the application methodology used, and many other factors.

Common failure modes encountered are often associated with thin films and the water susceptibility of the "tailing solvents" used in the formulation, occluded water caused by the use of active solvents producing fogging and cloudiness at application, and others. In acid-modified solution-vinyl systems, reaction with basic pigments will cause viscosity increases and possibly gelation in the can. Other problem areas leading to failures include the "strength" of the solvent system, temperature of the coating solution at application, interaction of solute binder polymer with certain pigment particles, and interaction of some pigment particles with other pigment particles.

Typical failure modes for lacquers include production of cloudiness during application (blushing), use of improper (nonsolvent) thinner, "fisheyes" (a surface tension problem), lifting of solvent-sensitive undercoats, and delamination from overcoating sanding sealers containing excessive sterates, among others. Coating softness is often related to the inclusion of nonsolvents entrapped in the film if their evaporation or migration rate is less than the true solvents for the coating system. To address this problem, the coating formulation will often have a small "tailing" of slow-evaporating true solvent to allow the escape of these nonsolvent diluents.

Because of the large amounts of solvents required and the typically low solids content, this type of coating system is not considered to be environmentally friendly. As such, lacquers are not as popular as they were in the past. Most states have enacted laws that control the maximum value of the volatile organic content (VOC) of the paints, and this has greatly limited their use.

Oxidative binders are polymers that usually require the pressure of atmospheric oxygen to cross-link sufficiently to form a strong film. Paints based on unsaturated vegetable oils such as linseed, soya, tung, tall oil, and others as well as modified vegetable oils, such as alkyds, fall into this category.

These coatings require metal catalysts called dryers to be included in the formulation. These dryers assist in the curing mechanism by increasing the coating's ability to react with atmospheric oxygen. A common failure mode for some alkyd coatings containing organic pigment would be a slow or nondrying paint after application. This occurs when dryers are either left out at manufacture or prematurely bound. In-can aging will allow adsorption onto the organic pigment particles, causing a loss of activity before application. Some carbon blacks are particularly susceptible.

Increased viscosity within the can is often caused by reaction with the oxygen contained in the air space above the coating. Frequently, with highly reactive oxidative binders, a small amount of inert gas may be placed in the head space of the can prior to shipping. Skinning and gelling are problems frequently encountered with this type of system. Retardation is controlled by the use of additives such as volatile ketimines. These volatile inhibitors interfere with the cross-linking mechanism, thus extending the life of the coating material after the can has been opened. Often, upon reopening a can of an oxidative type of coating, one will notice that a vacuum has developed. This is due to the reaction with (and consumption of) the oxygen that was in the air in the head space of the can.

Moisture-cured binders constitute a class of organic polymeric materials that require water vapor from the air to cause polymerization. While the most common of these are the moisture-cured urethanes, epoxies cross-linked by ketimines form another important class of moisture-cured coatings. Inorganic silanol binders, found in many zinc-rich systems, must have water to complete the hydrolyzation required in forming the cured inorganic silicate binder. Typical failure modes include application of the coating in conditions providing insufficient moisture to complete the cure. Application to surfaces that are damp or excessively wet can create bubble formation in urethanes. Overcoating inorganic zincs before complete hydrolyzation interferes with curing by stopping the reaction with moisture. This produces a zinc-rich primer layer with low tensile strength. Such films will often fail by cohesive failure within the inorganic layer, especially after application of an epoxy that shrinks slightly on curing.

Failures associated with thinners that contain water as a contaminant present a different kind of problem. For urethane coatings, inclusion of excessive water in the coating matrix will generate gas bubbles of carbon dioxide caused by reaction with the isocyanate groups. In a worst case, the applied coating will be rough with bubbles through the film. In slight contamination cases, this will be evidenced by viewing a chip of the coating from the side through a microscope. Small bubbles will be seen through the coating thickness. When the bubbles are mostly located at or near the interface, there is probable cause to suspect application over a damp surface. Water picked up on the pigmented side of a two-part urethane during the pigment-grinding process during manufacture is a common problem. Water analysis of the polyol side may reveal the source of the problem.

Water contamination introduced into an ethyl silicate binder can cause premature gelation and shortening of the pot life. Water pickup in zinc and aluminum-metal-containing coatings often produces gas of sufficient pressure to explode the container.

Chemically reactive cross-linking binders include all two-part systems. This includes epoxies and urethanes that have appreciable reaction rates at room temperature as well as single-package, cross-linking systems that require heating or some other energy source to increase the reaction rate significantly and allow a cure to be attained. Some systems will contain all the reactive polymeric binder precursors that cross-link with each other to produce the final film. Some systems may generate the required energetic cross-linking specie by a reaction brought about by an outside energy source such as ultraviolet (UV) radiation, electrodeposition, or high-energy electron beams.

Ambient-cure, two-component, or catalyzed binders such as epoxies and urethanes require a proper mixing ratio to allow the finished film to have its desired properties. Improper ratio mixing can lead to a host of final film problems. These problems include inadequate curing, brittleness, loss of extensibility, loss of chemical resistance, early extensive chalking, and many more. Off-ratio coating systems may be investigated using GC/MS pyrolysis [*1*].

Epoxies are often cured by amine functional polyamides, amine adducts, or aliphatic amines. Polyamides, being manufactured from long-chain fatty acids, are very aliphatic in nature and, typically, not particularly soluble in the epoxy side. Because of this poor solubility, it is often necessary to allow extra time after mixing for the reaction products to gain solubility characteristics more closely related to each other. This extra time is called the "induction period" or "sweat-in time" and allows time for the two resins to partially co-react. The partially reacted resin solution eventually changes the solubility characteristics of the binder system sufficiently to completely solubilize all resin components. A failure to reach complete solubility will lead to "zone curing" with macro islands of unreacted polyamide and potentially unreacted epoxy resin. Additional failure modes include osmotic blister formation (where the low molecular weight amine is the solute, with condensed water being the solvent), increased amine carbonate formation and exudation to create intercoat delamination problems, film brittleness, poor weatherability, and others.

Application of amine and polyamide systems in cold weather can present future delamination problems. In cold weather, when the epoxy-amine reaction slows down, the amine reaction with carbon dioxide and water vapor from air does not slow very much. The formation of an amine carbonate "bloom" develops on the coating surface. Additional amine carbonate within the coating matrix formed during spray application exudes to the surface. This leaves a weak boundary layer on the surface. When overcoated, the insoluble "greasy" amine carbonate will not allow adhesion of the next coat and usually results in delamination in less than a year. The interface will be moisture sensitive and potentially provide the solute for osmotic blister formation. The author has found a simple test to evaluate for the presence of the amine carbonates. This is done by applying a drop of 6 *M* hydrochloric acid to a suspected surface while watching the edge of the drop under a microscope. The HCl will liberate the carbon dioxide at the edge of the "wetting front" as the droplet wets the surfaces. The bubbles of gas can be seen in

the edge of the drop of liquid. The experiment should be conducted under a microscope since the reaction is rather fast and because often only a small amount of gas is liberated. The gas may present itself as a tiny bubble within the drop of acid solution. To test the amine side of the curing agent for carbonate salts, add about 1 mL of the resin component to a test tube. Tilt the test tube at about 45°, add a drop of the 6 *N* HCl, allowing it to run down the inside of the tilted tube, and note the production of any foaming carbon dioxide at the acid solution/resin interface. The amount of foam produced is a quantitative indication of the amount of carbonate existing. Grinding pigment into the amine side, in open tanks, often introduces the carbonate.

Heat-activated binders have a cross-linking reaction rate that is too slow at room temperature to allow complete cure. These systems require heating to provide a forced cure. This is true for liquid systems as well as for most thermoset powder coating systems. Typical failure modes include abnormal brittleness, discoloration, lack of design physical properties, lower chemical resistance, and other problems. Causes may stem from formulation problems such as batch-to-batch variation in catalyst level or incorporation, as well as problems associated with variable temperatures within the pass-through ovens or heating equipment. Low temperatures caused by variations in metal heat capacity due to variations in metal mass of a coated part are seen often in powder coating systems as producing curing anomalies. Since the cured coatings will typically have elevated glass transition temperatures, T_g, the differential scanning calorimeter (DSC) is the instrument of choice in determining quality of cure [*8*].

Nonthermal, high-energy-cured binders require an energy source other than heat. These coating systems are typically employed on fast-moving, automated industrial lines. The coatings include both ultraviolet radiation curing systems as well as electron and other high-energy beam curing. Because the energy source must be "felt" through the polymer layer, UV-cured systems must be fairly transparent to the energy source and preferably have little or no pigmentation. However, UV-curable colored inks and coatings are commercially available. This usually necessitates that the films be of low DFT.

Inorganic Binders—Those Based on Noncarbon Polymers

Inorganic coatings are those that do not rely on carbon as the primary atomic composition of the polymer. These include those systems that ultimately end up with an inorganic binder after application. The most common include zinc-rich systems using alkali silicates as the binder. Generally speaking, inorganic coatings are formed from the oxides of specific elements. The silicates are formed from the oxides of silicon. Cement coatings and linings for water pipes rely on the oxides of calcium or variations thereof. Some high-temperature coatings used in flue gas desulfurization stacks are based on calcium sulfate.

A different class of inorganic coatings are those that are chemically reacted onto a metal surface. These include the colored anodized coatings commonly seen on aluminum window and door frames, precipitated zinc and iron phosphate coatings used as anticorrosives on pretreated steel, and acid phosphate treatments to zinc and galvanized surfaces, among

TABLE 1—Frequently used ASTM standard test methods for evaluating paints for specific properties.

B 117	Test Method of Salt Spray (Fog) Testing
D 522	Test Methods for Mandrel Bend Test of Attached Organic Coatings
D 523	Test Method for Specular Gloss
D 570	Test Method for Water Absorption of Plastics
D 610	Test Method for Evaluating Degree of Rusting on Painted Steel Surfaces
D 660	Test Method for Evaluating Degree of Checking of Exterior Paints
D 661	Test Method for Evaluating Degree of Cracking of Exterior Paints
D 662	Test Method for Evaluating Degree of Erosion of Exterior Paints
D 714	Test Method for Evaluating Degree of Blistering of Paints
D 772	Method for Evaluating Degree of Flaking (Scaling) of Exterior Paints
D 869	Test Method for Evaluating Degree of Settling of Paint
D 968	Test Method for Abrasion Resistance of Organic Coatings by Falling Abrasive
D 1014	Method for Conducting Exterior Tests of Paints on Steel
D 1186	Method for Nondestructive Measurement of Dry Film Thickness of Nonmagnetic Coatings Applied to Ferrous Base
D 1200	Test Method for Viscosity of Paints, Varnishes, and Lacquers by Ford Viscosity Cup
D 1210	Test Method for Fineness of Dispersion of Pigment-Vehicle Systems
D 1400	Test Method for Nondestructive Measurement of Dry Film Thickness of Nonconductive Coatings Applied to a Nonferrous Metal Base
D 1475	Test Method for Density of Paint, Varnish, Lacquer, and Related Products
D 1653	Test Method for Water Vapor Permeability of Organic Coating Films
D 1654	Test Method for Evaluation of Paints or Coated Specimens Subjected to Corrosive Environments
D 2196	Test Method for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield) Viscometer
D 2244	Test Method for Calculation of Color Difference From Instrumentally Measured Color Coordinates
D 2621	Test Method for Infrared Identification of Vehicle Solids From Solvent-Reducible Paints
D 2697	Test Method for Volume Nonvolatile Matter In Clear or Pigmented Coatings
D 3363	Test Method for Film Hardness by Pencil Test
D 4060	Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser
D 4212	Test Method for Viscosity by Dip-Type Viscosity Cups
D 4214	Test Methods for Evaluating the Degree of Chalking of Exterior Paint Films
D 4400	Test Methods for Sag Resistance of Paints Using a Multinotch Applicator
D 4417	Test Methods for Field Measurement of Surface Profile of Blast Cleaned Steel
D 4541	Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers
D 5179	Test Method for Measuring Adhesion of Organic Coatings to Plastic Substrates by Direct Tensile Testing
G 8	Test Method for Cathodic Disbondment of Pipeline Coatings
G 14	Test Method for Impact Resistance for Pipeline Coatings (Falling Weight Test)
G 42	Test Method for Cathodic Disbonding of Pipeline Coatings Subjected to Elevated Temperatures
G 95	Test Method for Cathodic Disbondment Test of Pipeline Coatings (Attached Cell Method)

others. Typical failure modes with these types of coatings will include underfilm corrosion and spalling of the coating, especially with cement that has become carbonized from reaction with carbon dioxide and, therefore, lacks the higher pH required to disallow corrosion of embedded steel. Corrosion testing methods such as given in ASTM B 117 (see Table 1) are used often to determine coating quality.

Precipitation-type coatings are usually done from a water solution. Because of this, the surfaces must be able to be wet-out by the water solutions. A typical problem is "splotchiness" caused by incomplete thermodynamic wetting of the substrate. This lack of wetting disallows water-based chemical reactions that must occur at the metal interface. The reason for a lack of wetting is usually from oil or other low-energy contaminants on the surface. Investigation of the precleaning system is indicated in these cases. Surfactants are usually added to overcome this problem, but these may then cause an even worse problem if they are not totally removed. One must remember that surfactants are called "surfactants" because of their ability to displace, usually thermodynamically, most adsorbed species on the surface of the substrate. When overcoating a substrate that has been wet with surfactant, these surfactants must be displaced. This can often be difficult or impossible and often leads to eventual delamination or water sensitivity. A short-term test frequently used is the Hot Water Boil Test. This is also called the "Crock Pot Test" since a standard kitchen electric crock pot has been found to work very well. Samples are cut from coated specimens that have been through the cleaning system. These are placed in the crock pot under deionized water for 24 h (or less, depending on type of coating), and the coating is evaluated against a standard of known cleanliness.

Metallic Coatings

Metallic coatings are very thin layers of pure metal, usually applied to a substrate for appearance, modification of ware characteristics, corrosion protection, or to disallow the transport of migrating gas molecules through plastic film. They are important because of their ability to modify physical properties of the substrate such as stopping the migration of oxygen, carbon dioxide, and other small molecules through plastics. An example most are familiar with is the shiny metallized coatings seen on food wrappers containing oxidizable vegetable oils. It is usually assumed that these shiny packages are for "aesthetics only," however these thin metallized films serve to stop the migration of oxygen into the food package. With the trend to eat more unsaturated oils in our foods, the oxygen would react with the unsaturated bonds in the oils to produce a rancid taste. This is associated with the product being old and stale. The bad taste is due to the formation of aldehydes during the oxidation process.

Failure Modes Associated with the Pigment System, Carrier System, or Additive Package

Some common failure modes associated with the pigment system include: heavy settling; flocculation; lack of wet-out during manufacture; insufficient grind or dispersion development; adsorption of additives such as driers, UV stabilizers, and surface-active agents during storage; and poor color stability with some pigments. Improper use of the anatase titanium dioxide can lead to chalking. Accelerated ageing tests of the formulated coating usually include storage at elevated temperatures with intermediate observations of settling and grind measurements.

The carrier system assists the binder system in forming a film and in developing adhesion during application. For liquid coatings that are sprayed, rolled, brushed, flow coated, or dipped, the viscosity must be within certain limits dictated by the application equipment, final film build desired, and ambient conditions. Additionally, there must ultimately be intimate contact between the binder polymer and the substrate. While this may appear to occur automatically and instantaneously, it does not. Development of adhesion between binder polymer and the substrate is a time-dependent function. Thermodynamic wetting is controlled by the energetics in existence between the actual surface encountered on the substrate by the coating system. Thermodynamic wetting is a necessary, though not sufficient, condition for adhesion. Unfortunately, since adhesion development is a dynamic process requiring time for the many "molecular realignments and adjustments" to occur as well as the displacement of molecular species lightly bound to the substrate, high-solids coatings with little or no solvent have a formidable job before them. Displacement of surfactant-type molecules at the interface will usually present a severe challenge and frequently present delayed adhesion failures.

There are always adsorbed species on the surface. Depending on the "sticking" strength of the adsorbed surface species, the binder may not make intimate (molecular) contact with the substrate as its viscosity is increasing to a gel. Adsorbed species include such molecules as vapor-phase water, oxygen, and other gases from the air, oily contaminants, and surfactants from cutting oils or coolants. In thermodynamics, this sticking is related to the heat of wetting. Failure to displace these compounds often results in eventual adhesion problems. One of the roles of the solvent is to assist in wetting out the substrate by displacing the adsorbed species followed by deposition by the binder. The coatings formulator will design the solvent system to assist the polymeric binder in displacing any interfering adsorbed species. But, since desorption/adsorption is a time-dependent process, extremely fast solvents and viscous, high-solids systems may not be able to respond in the time during which the polymer system cures and approaches a gel state. Increases in viscosity after application also present additional problems. There must be sufficient time for adhesion to develop between the binder polymer and the substrate. In some instances, changes to the polymer backbone have been done to produce a more negative heat of wetting [5]. The use of additional mechanical energy as from brushing is always helpful. It is for this reason that brush striping of welds in tanks and critical areas is often required prior to spray application of the first coat.

Solvents are the most common of the paint system carriers. Typical problems encountered might include use of the wrong solvent, allowing water to contaminate proper thinners that have been stored outside, transfer of solvents to oily or contaminated containers, etc. Water, which has been drawn into a solvent container due to temperature changes, is a common work-site occurrence.

Air suspension of powders is an example of a nonliquid carrier system. Powder coatings are usually applied electro-

statically by fluidizing the powder with compressed air in a porous bottom chamber. The air-suspended particles are then drawn into an air stream via a venturi nozzle and transported to the point of application. Surfaces being powder coated may or may not be heated before application. With application to hot substrates, the powder melts and flows to produce a relatively thick coherent film. Depending on melt viscosity, flow characteristics, gel time, and thermal transfer characteristics of the melted polymer, air bubbles may be in evidence throughout the film. Due to the poor thermal transfer of the powder coating, the bubbles will be concentrated closer to the heat source, i.e., the substrate. These bubbles have not been a problem with fusion-bonded epoxy (FBE) pipe coatings other than to cause a decrease in lateral cohesive film strength. Failure modes common to powdered pipe coatings stem from the use of wet air, plugged ventures and spray nozzles, and irregular heating of the metal surfaces for various reasons. Long-term adhesion problems may develop when application to the steel surfaces occurs at too low temperatures. High steel temperatures favor enhanced thermodynamic wetting. Variations in adhesion often follow variations in steel surface temperature.

When powder coatings are applied to cold surfaces followed by heating through conveyor ovens, film build is usually limited to no more than 2 to 4 mils. Because of the short time allowed for flow and wet-out to occur, surfaces must be very clean and receptive to the applied coating. Typical failure modes are associated with surface pretreatments, poor adhesion over unclean surfaces, contamination with other noncompatible or off-color powders from the same application system, compatibility with specific surface pretreatments, "wet" air used as the carrier, as well as curing difficulties resulting from catalyst deactivation or poor incorporation during extrusion. Gel particles may result with some catalyst systems.

It is not practical to assume that the practitioner will have experience in all areas necessary to address the multitude of potential problems. Knowledge of application equipment, an in-depth chemical knowledge of the formulations and specific curing mechanisms and the physics of adhesion including the energetics controlling adsorbed molecular displacement, among other things, are required to thoroughly understand the potential problems one will encounter in the field. This should be developed through continued study, close observation, and by asking questions.

Tapes and extruded polyolefin thermoplastic coatings are popular pipe coatings. Sheeted rubbers find use on the risers of off-shore platforms and as acid tank linings. These will have specific failure modes. Rubber must be vulcanized in ovens after application to the tank wall or pipe. Failure modes usually will be associated with the improper cure of the polymer. This could stem from catalyst inactivation caused by the use of improper curing temperatures. Tapes of PVC with various types of adhesive binders are popular pipe coating materials. These may be applied in the cleanliness of a factory or as a "railhead operation" at the point of pipe construction or over the ditch. Extruded polyethylene and polypropylene pipe coatings are usually applied in a factory setting. Sheeted rubber coatings are frequently applied to the interior of carbon steel tanks that will see acid service. This is done both in the fabrication facility and in the field when it is possible to provide sufficient heat to cure the vulcanizable adhesives and coatings used. A common problem often encountered with these systems is the inadvertent inclusion of air bubbles or air pockets under the coating material. Bubble inclusion followed by eventual underfilm corrosion and perforation of the steel is a major failure mode for this type of coating.

Was the Specified Coating Material Used?

Often it is necessary to determine that the specified coating was used. Typically, Fourier transform infrared (FTIR) analysis of the binder is the analytical method of choice due to the widespread availability of the instrumentation. There is often considerable difficulty in gaining a positive identification of the coating due to interference from the pigments that produce an instrument response added to that of the polymer. The presence of silicates in paints is very common. A silicate peak often obliterates an informative section of the FTIR scan used to identify the polymer in question. Additional problems can stem from the specific technique used. The use of a "diamond anvil" attachment to a FTIR microscope has proven very beneficial in getting good polymer scans in the presence of interfering pigments but on rare occasions introduces some uncertainty when the binder is not totally homogeneous or well dispersed. An expected peak may appear to be missing. A good example is the presence of a crystalline, nonsoluble cross-linker containing the cyano functional group in a fusion-bonded epoxy powder coating that is not seen using the FTIR diamond anvil in microscopic transmission mode but that is seen using the typical FTIR attenuated total reflectance (ATR) mode of surface analysis. GC/MS techniques provide a definitive analytical technique for identifying the coating used years after an application [*1*].

Was the Coating Material Properly Formulated and Manufactured?

Determining the "as applied" quality of a coating years after application can be a difficult task in some respects. On the other hand, it is usually surprising to most that the solvents used in a coating typically remain in the applied coating material for many years. A good example is the trapping of alcohols in cured epoxy coating systems for years after application. Normal-butanol, a very common solvent used in epoxy-polyamides formulations, can be extracted three to five years after application. High-molecular-weight oxyalcohols and glycols are also present for long times and are often found as the solute in an osmotic coating failure. Gas chromatography using thermal extraction (TE) with liquid nitrogen "cryotrapping" before starting the GC run and a mass spectrometer (MS) for the detector (GC/MS) allows for a positive identification of trapped solvent molecules. The vapor transmission coefficient within the cured coating system dictates the rate of solvent loss after application. The technique is also very useful for identifying the generic type of coating used years after application by pyrolyzing a very small coating chip at a higher temperature. By doing this in a stream of helium and trapping the fragments with liquid nitrogen, an analysis of the fragments will allow one to identify the original polymer [*1*].

Quality in the manufacture of the coating products includes both the proper formulation for use in the environment intended as well as the eventual commercial manufacturer. There is usually a lengthy testing program required to evaluate the coating formulation before a product is commercialized. A few typical failures seen in the formulation and manufacture include systems formulated to contain low vapor pressure, water-soluble solvents in coatings to be used under water, formulation without required UV or thermal stabilizers for exterior coatings, gelation of acidic binders by reaction with basic pigments, loss of dryer catalysts from a oxidizable coating system, inclusion of carbon dioxide and water vapor into the amine side during the manufacturer of an adduct for a two-part catalyzed coating, and failure to exclude water contaminants during the manufacture of the nonisocyanate side of a urethane coating system.

WHAT WAS THE DESIRED PURPOSE OF THE COATING?

Before designing the test regime to evaluate a specification or starting the investigation of a failed coating, the analyst should ask why the coating was applied. Often it will be intuitive or would be stated in the specification. The design of the testing and evaluation program should include elements encompassing these objectives. Table 1 lists some of the ASTM standard test methods used to evaluate a coating's specific serviceability relative to a particular property. Table 2 lists some of ASTM's standard practices for accomplishing the objectives.

Coatings provide a renewable surface and allow the engineer to use materials that are more economical or provide a physical characteristic not attainable from the uncoated surface. While coatings frequently provide a variation in appearance, most coatings serve to protect more than to beautify. When the protection is not provided for the full design life of the coating, including the maintenance of all expected and desired protective properties, a coating failure has occurred. Frequently the coating will be evaluated for a particular service through a series of tests. These evaluation programs are designed to assist in predicting failure modes and to assist in the preparation of specifications. Problems often develop when the service does not match the initial testing program.

A major reason for applying coatings to many different types of substrates is to protect the substrate from deterioration. Coatings on steel, when applied properly, have the ability to stop corrosion in hostile environments for a period of time. Coatings applied to wood have the ability to prevent fungus growth and rotting, even in damp environments. Hard metallized coatings protect softer metals from wear. Highly active metallized coatings such as zinc and aluminum have the ability to prevent corrosion of steel in adverse conditions [2]. When coatings are applied to protect the substrate and the substrate sustains premature damage, a coating failure has occurred. Test regimes usually address the perceived problem. Sophisticated a-c impedance and d-c polarization techniques have the ability to measure actual corrosion currents and represent a very sensitive test method for metal substrates.

TABLE 2—Frequently used ASTM standard practices for evaluating paints for specific properties.

D 609	Practice for Preparation of Cold-Rolled Steel Panels for Testing Paint, Varnish, Conversion Coatings, and Related Coating Products
D 870	Practice for Testing Water Resistance of Coatings Using Water Immersion
D 1006	Practice for Conducting Exposure Tests of Paints on Wood
D 1150	Practice for Single and Multi-Panel Forms for Recording Results of Exposure Test of Paints (discontinued)
D 1730	Practices for Preparation of Aluminum and Aluminum-Alloy Surfaces for Painting
D 3002	Practice for Evaluation of Coatings for Plastics
D 3925	Practice for Sampling Liquid Paints and Related Pigmented Coatings
D 3960	Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings
D 4414	Practice for the Measurement of Wet Film Thickness by Notch Gages
D 4708	Practice for Preparation of Uniform Free Films of Organic Coatings
D 5162	Practice for Discontinuity (Holiday) Testing of Non-Conductive Protective Coating on Metallic Substrates
G 53	Practice for Operating Light- and Water-Exposure Apparatus (Fluorescent UV-Condensation Type) for Exposure of Nonmetallic Materials

Coatings are often applied to the inside surfaces of pipes, tanks, plastic and paper food packages, food and beverage cans, and rail cars to protect the contents from contamination and/or spoilage. This contamination may originate from the metal container, which leads to discoloration of the product by allowing metal ions to enter. Contamination in the form of bacteria or degrading reactive gases are frequently a problem in food packaging. Tank coatings may fail by allowing components of the coating to migrate into the products carried within the tanks. Loss of coating components will then lead to coating shrinkage that will stress relieve in various ways leading to failures by cracking, increased osmotic activity, etc., depending on the products carried and the coating polymer fragments remaining. A coating failure that allows product contamination is usually very costly.

Coatings are frequently applied to enhance a substrate's appearance. Because of this, any undesired change in the coating's visual attributes will constitute a coating failure. This would include not only changes in color, gloss, and texture, but appearance failures due to growth of algae and mildew as well. Failure modes related to a loss in aesthetics are usually adverse reactions to the environment, often due to ultraviolet radiation or delamination of the coating.

Small molecules such as water and the acidic gases carbon dioxide, hydrogen sulfide, and sulfur dioxide have the ability to migrate through a polymer film. When this occurs, the possibility of corrosion of the substrate is great. Frequently, coatings are used to interfere with this process. The rate at which these small molecules can pass through a coating or polymer membrane is called the vapor transmission coefficient for that specie. Metal coatings applied to food wrappers inhibit or stop migration of oxygen, thereby maintaining freshness. A failure to prevent these molecular migrations in an amount based on the original design parameters constitutes a coating failure. Often this failure mode is closely related to cross-link density or changes in cross-link density after coating degradation.

Coatings are applied to stair treads and slick surfaces to provide nonslip characteristics. On the contrary, internal pipe coatings should be very smooth so as to provide decreased resistance to flow. This allows increased volumes of fluids with less pressure drop and lower power requirements for the pipeline. Many coatings provide abrasion resistance to a substrate, thereby increasing the substrate's life indefinitely since coatings are a renewable entity. Failure of the coating to accomplish any of these design goals constitutes a coating failure.

Coatings are frequently applied to metal substrates to modify electrical flow characteristics. Coatings are naturally dielectric, though conductive pigments and additives may decrease internal electrical resistance for special requirements. The electrical resistance becomes an important attribute in accomplishing a particular circuit requirement. A very good example are those coatings applied to metal surfaces that are placed under cathodic protection such as underground pipelines, metal bulkheads at a shoreline, ship bottoms, offshore underwater structures, as well as internal tank linings. ASTM G 8, G 42, and G 95 (see Table 1 and Ref *3*) are methods for evaluating the cathodic disbondment properties of coatings. Because of the generation of large concentrations of hydroxyl ion at coating defects, saponification of the coating or steel pretreatments can be a dominant failure mode with some coating systems.

Conductive coatings are used to dissipate electrical charge. These are found in laser printers and some copy machines. Conductive coatings are also applied to bags, plastic mats, and other articles used around electrical equipment sensitive to the discharge of static electricity. A failure to provide the desired low electrical resistance or conductivity over its planned lifetime constitutes a coating failure.

For materials that expand and contract extensively with changes in absorbed materials such as water and carbon dioxide, minimizing absorption will allow the substrate to remain dimensionally stable. Wood, when "dry," is about 10 to 15% water. Depending on the type of wood, absorption of water, especially through open-end grain, causes huge changes in the size of the piece of wood. Other characteristics such as flexibility, warping, and cracking are a common occurrence when wood coatings fail. The peeling of coatings on wood usually starts at some break in the film and slowly radiates from the site of moisture egress. As moisture enters the wood, it expands greatly and pulls the coating from the surface. As it dries out, the wood shrinks. This continual expansion and contraction is a major source of problems for wood coatings.

Paper products must be protected from moisture pickup to maintain strength and integrity. Paper cartons containing milk and other food products are usually protected by surface coatings of wax, polyethylene, or vinyl thermoplastics. Sizing or starch-type coatings are frequently applied to paper to provide a degree of stiffness.

While gloss is frequently considered an aesthetic property, coatings that have the ability to reflect or absorb specific wavelengths of light are functional coatings. Pigmented coatings engineered to reflect very little radiation are often applied to thermal adsorption devices such as solar heat exchangers. Coatings with adsorption efficiencies approaching 95% have been developed. Changes in reflection or adsorption characteristics over the coating's planned life span constitute a coating failure.

Coatings containing voids or small bubbles have the ability to adsorb mechanical wave energy such as sound. Changes with time in these adsorption or dampening abilities usually constitute a coating failure. Some of these unique physical properties are impacted by the adsorption of liquids such as water from condensation and may be the subject of test programs when evaluating this type of failure. Knowledge of the physics of wave energy transmission and point reflection through elastic media is necessary to design test programs evaluating these parameters.

HOW WAS THE COATING APPLIED?

Many coating failures can be traced to problems associated with the procedures surrounding the coating's application. For this reason, each step of the process must be considered. Getting a particular coating applied can be thought of as having been accomplished through a series of steps with multiple responsibilities. These broadly include the following:

1. Preparation and follow through of the specification.
2. Preparation of the surface/substrate.
3. Physical application techniques and equipment.
4. Third-party inspection.

The specification, type of coating being applied and its particular curing requirements, variations in ambient weather conditions, variations in the condition of the substrate, surface preparation techniques, pretreatments, equipment used during the application, the quality of third-party inspection as well as the applicator's knowledge and ability all play a major role in getting the coating properly applied.

Preparation and Follow Through of the Specification

The specification should serve as the "blue print" for getting the coating properly applied. Its existence implies that someone has surveyed the site to determine any abnormalities that might exist, evaluated the service requirements, reviewed the particular problems unique to the structure and service demands, identified a particular coating with the required service characteristics through prior testing, and provided an adequate application procedure that, theoretically, will meet the use requirements. The specification assists the applicator in knowing what is expected of him and serves as a legal document in times of dispute.

Frequently a coating will be specified by a specific manufacturer's product numbers. Failures in the specification, either in the type of recommended coating or the application procedures, can result in early failure. As such, the specification must be reviewed when investigating a coating failure. Coating materials may have been used that were not on the approved list. Most applicators are not in possession of proper knowledge to make substitutions and usually do not want that responsibility. Coating failures in many forms have resulted from attempts to circumvent the specification. Analysis of very small coating chips by FTIR or GC/MS and com-

pared with known samples can demonstrate compliance or lack thereof [7].

Before specifying a particular coating system, it is usual to evaluate specific candidates in a test program that closely simulates the use environment. This is accomplished either within the owner's organization or by subcontracted third part testing organizations. While most of the required test procedures are found in Volumes 6.01 through 6.04 of the *Annual Book of ASTM Standards*, specific custom-designed procedures may be desired.

Often a particular coating material will require specific application procedures dictated by its formulation. The coating manufacturer is in the best position to determine this since he is knowledgeable about the components of the coating. Requirements placed on the curing regime, mixing times with requisite induction periods, strainer mesh sizes, and other requirements will be specified by the manufacturer.

Preparation of the Surface/Substrate

The quality of the surface preparation done prior to coating application will strongly influence the life of the coating. Some contaminants are very harmful and lead to early failure in certain services. Some contaminants can be tolerated, and, while coating life may be somewhat adversely effected, long-term longevity can be realized. Displacement of some surface contaminants may be addressed by variations in the ability of the solvent system to affect coating wet-out. Contaminates that interfere with adhesion or promote underfilm corrosion are particularly troublesome to paints. There are potential problems with all types of surface preparations. The Steel Structures Painting Council (SSPC) has produced specifications addressing some of the most common surface preparations for steel [6]. These specifications will usually dictate the specific surface cleanliness required for service and should reflect that used during the original test sequences.

For coatings that have an extended design life, as with automobile bodies, the surface preps are extremely sophisticated. Unique electrodeposition coatings require a very clean and totally wet-out surface. Coating failures on this scale have resulted in multimillion dollar claims. Chemical pretreatments present potential failure problems as well. Cleanliness of the substrate and its impact on adhesion is the topic of many testing programs. But since one must be looking at the surface at a depth of no more than a few angstroms, the analytical techniques required include auger spectroscopy and X-ray photoelectron spectroscopy (XPS). The use of EDX to analyze a "surface" is not proper because the area being analyzed will include a depth well below the surface where "adhesion" will occur. While this technique is usually defined as a surface technique, it does penetrate well below the actual surface encountered by the coating as it attempts to "wet-out" the substrate.

Improperly operating equipment is a major source of coating failures. A very common problem is the abrasive-blast-cleaning air compressor that passes oil. Oil contamination can be a long-term, serious problem with certain coating systems. While pure aliphatic oil residues, being low-energy compounds, are usually displaced by the active solvents of the coating system such as ketones and esters, oils that contain surfactants present a serious problem. Adhesion between the binder of the coating and the substrate takes time to develop. It is highly probable that adhesion problems will develop with the egress of water vapor if the interface has been contaminated with strong surfactants and the solvent system does not have time to displace them before the coating gels and its glass transition temperature reaches ambient temperature. Analysis of the interface surfaces by XPS can allow a definitive identification of the structure of the molecules forming the interface and is required to identify the locus of failure.

Profile and surface conditions existing at the time of coating application are difficult to evaluate after a coating has been in service for a while. Frequently, though, it is necessary to inspect the substrate under a coating. Paint may be removed by using commercial paint stripper, allowing inspection of substrate profile and the current surface condition. This may include the presence of corrosion products, or mill-scale deposits may be found where the specification calls for complete removal. While the actual profile is not as critical as the original molecular contaminants that could interfere with the thermodynamic wetting process, one can gain insight into the history of the surface being inspected.

For submerged services, a "white metal" abrasive degree of cleanliness is usually specified. If a metal sample may be removed and is bendable, the sample may be subjected to extreme cold, as with liquid nitrogen or carbon dioxide followed by rapid bending. The coating will usually pop from the substrate if chemical bonding has not occurred, allowing a clear measure of the debris that remained at the time of application.

Physical Application Techniques and Equipment

The physical application techniques employed as well as the equipment used can lead to many types of coating failures. Coating defects can range from pinholes caused by small compressed air bubbles whipped in during high-speed stirring and applied by airless application systems, to curing problems originating from improper ambient field conditions, off-ratio mixing, or inclusion of water contaminants from "bad" solvent. Some defects such as orange peel, sags, and runs will be evident at the time of application, but improper curing of a coating may not become evident until a failure occurs months or years later. The analytical techniques useful in evaluating off-ratio mixing of catalyzed paints depends on the coating matrix, but typically include thermal methods such as differential scanning calorimetry (DSC), FTIR, gel permeation chromotography (GPC)/high-pressure liquid chromatography (HPLC) of solvent extracts from the failed coating, and GC/MS are typical analytical methods for evaluating cure.

The specific application technique will often present typical failure modes. Test programs that evaluate a particular coating before it is specified will usually utilize the expected application techniques. Application by spray, roller, brush, flow coater, dipping, or trowel requires that the coating material have certain physical properties. Ambient conditions expected at the time of application should be considered. Application may use electrostatics with some powders and liquid paints.

Was the coating properly cured? Was the temperature and relative humidity in the required range? Some moisture-cured ethyl-silicate, zinc-rich systems as well as moisture-cured epoxies and urethanes require that there be sufficient moisture available to allow binder-curing reactions to occur. Overcoating these coating systems before there has been sufficient water pickup can lead to premature coating failure due to insufficient coating strength development. Too much water can cause blushing with high flash lacquers.

The curing of a coating is usually by chemical reaction with the polymer precursors in the paint. All physical laws controlling chemical reactions will be in effect. This means that the reaction rate will be controlled by the substrate temperature since the heat capacity of the coating will usually be considerably less than the substrate. Potential side reactions with atmospheric constituents such as water and carbon dioxide may be a problem with some binders. For moisture-cured systems such as urethanes, epoxies, and ethyl silicate systems, air that is too dry will interfere with polymer curing. Excessive humidity may leave surfaces with a microscopic layer of water. With solvent-borne paint systems, this may not be as critical as with the super-high solids or 100% solids systems. The solvent system is usually engineered to assist in moisture removal by displacement, desolution, and selective azeotrope formation. Coatings that cannot displace these interfering surface-adsorbed species with properly engineered solvent systems may experience delamination shortly after application. With most coating systems, this may be demonstrated by the addition of thinners of varying "strengths" and noting the delamination sensitivity caused by water vapor. When a coating delamination problem exists with a particular coating system and the "adhesive" qualities may be enhanced by adding active thinner only, one may suspect problems with the thermodynamic wetting of the substrate.

Third Party Inspection

An important part of the professional application program will often include third party inspectors. These are usually required by the owner and serve as monitors and record keepers for the job. Should a failure occur in the future, the records frequently provide the only link to the daily happenings. Data will include paint batch numbers, weather data for each day, humidity and temperatures, wet- and dry-film builds, the thinners used, logging of equipment problems, names of operators, and a multitude of other data. Very important information useful to the solution of coating failures is often found in the inspection reports.

WHAT EVIDENCE IS PRESENTED BY THE FAILURE?

To successfully diagnose the causes of failures in coating systems, the investigator must be fully cognizant of all of the factors affecting the coating's longevity. This includes; (1) a thorough knowledge of the chemistry of the coating systems being used; (2) factors affecting the cross-linking, cure, or film-forming characteristics of the binder; (3) factors affecting adhesion and potential adverse chemical reactions between the substrate, binder, and environment; (4) corrosion fundamentals and protective techniques; (5) potential formulation problems; (6) potential application problems; (7) the suitability of the specified coating for the service; and (8) the instrumentation that can provide sophisticated answers to the complex questions that exist.

It is rare for all of these disciplines to be found in a single individual. New coating polymers are being developed routinely and are being incorporated into coating systems. Their reaction chemistries both with the cross-linkers used to produce the final film and the interfering side reactions with ambient, local, or solvent species may produce unexpected results. Because of this, the successful investigator must be aware of his/her limitations and be willing to seek knowledgeable assistance when necessary.

Those with experience in the formulation of paints and coatings will often have a distinct advantage over others. Understanding the potential shortcomings of the polymers used, the problems forced by the use of environmentally friendly solvent systems, the functions of the additives, the physics of adhesion, and the limitations of the analytical "tools-of-the-trade" will assist in understanding failure mechanisms. Even still, the challenge is tremendous and true solutions may be elusive. It is important to know when to ask for help.

While the investigation of a coating failure requires all of the knowledge discussed, a systematic approach offers the best chance for a successful conclusion. Before beginning the investigation, it is important to follow a preconceived procedure that will ensure that each phase of the investigation is addressed. Since each failure may be somewhat different, there will be opportunities to veer from the path as evidence is produced. The investigation should contain the follow elements as a minimum:

1. Gather background information.
2. Conduct the field investigation.
3. Conduct the laboratory investigation.
4. Consider potential failure modes and test the hypothesis.
5. Report the findings.

Gather Background Information

Inquire as to the nature of the problem. While the first reports coming in from the field will usually lack details necessary for a definitive conclusion, they do provide a picture of the problem. There is little standardization of the descriptions of failures. As an example, coating delamination can occur at the interface or within the coating or substrate. The observer usually will know only that "the coating fell off."

Obtain a copy of the specification. This will provide insight as to potential problems perceived at the initial documentation. The type of coatings and typical failure modes will prompt additional questions.

Obtain relevant daily inspection reports. These will provide data as to the current weather conditions at the time, equipment malfunctions, types of paints used, as well as any problems encountered out of the ordinary. Batch numbers of the coating material will allow queries to the manufacturer as to similar problems that may have been seen with the coating in other situations.

Conduct the Field Investigation

Talk to the applicator if possible, not just the foreman. Inquire as to any recollections about the application. Was the weather at the time of application cold, wet, dry? What was the time of day, direction of surfaces, surface preparation, blast medium used, condition of equipment?

Ensure that field test instruments are properly calibrated. The data must be reliable and relatable to other data available from original testing done prior to specification writing and the coating manufacture.

Gather all relevant samples. Representative paint chips from the "bad" area should be matched with representative samples from a "good" area. Fluid from under blisters may be withdrawn with hypodermic syringes and stored in glass bottles. Empty cans, samples of shot/grit from the automatic abrasive cleaning machines, sample debris from the dust collector, liquid samples from degreaser/phosphating baths, etc. will hold clues to problems.

Perform adhesion checks if indicated. ASTM D 3359 (Test Methods for Measuring Adhesion by Tape Test) describes methods for determining the degree of apparent adhesion of the coating. Frequently, poor or marginal adhesion causes other problems to surface although the coating appears to be intact. Underfilm corrosion is a common occurrence when contaminants remain on the steel interface after coating application.

Inspect surface profile and cleanliness of substrate. The depth and intensity of the abrasive cleaning will determine whether the surface contains "new metal." Profile depth alone is not sufficient to describe the surface. For high-solids coatings with limited active solvents, wet-out of the interface, a requirement for the development of adhesion, may not be possible as the coating increases its viscosity to a gel. As the coating cures to a film and internal stresses began to grow across the outer surface, some coatings can literally pull themselves from the surface. The inability of the coating to encapsulate debris encountered on the surface exacerbates the problem and decreases its total adhesion.

Field test for cure by MEK rubs. This test is useful for catalyzed coating systems such as epoxies and urethanes, though not suited for alkyds or latex systems. If the coating can be resolubilized, there is a high probability that there is a problem with the curing. Off-ratio catalyzation, severe zone curing from inadequate induction time, and deactivation of one reactive component are but a few of the reasons for failure of the MEK rub test.

Photo document observations. Include relevant data in each photo. This might include the observation number, test location, film build, highlight of suspect area (both good and bad), and some point of reference. The point of reference might be a pencil, coin, or even the investigator's finger. Cracks in a tank lining may be 1 cm long or 1 m long. A photograph without reference may be impossible to distinguish against a background (wall) of white paint.

Observe all activity in the area that may impact coating application or longevity. When inspecting the coating facility, look about to determine if other activities may present problems. Is the grit blast machine near the degreaser? Is metal shot and grit getting into the phosphating bath, increasing the chance for leaving loose iron phosphate on the surface to be overcoated? Is automatic welding equipment nearby using silicon sprays as a wire lubricant. These have been the reasons for coating failures in the past.

Conduct the Laboratory Investigation

After gathering the samples, the analysis may be planned depending on the nature of the problem. In answering those questions posed before, some analytical laboratory work is usually required. Some of the instrumentation and the answers they provide may be summarized in the following discussions about each instrument.

Infrared analysis of coating samples is sometimes useful in determining whether the specified coating was used. Operator technique is very important in obtaining totally definitive information, and results are often marginal. The method is very useful in testing the coatings prior to application when there is a desire to ensure compliance. Microscopic FTIR provides greater sensitivity when analyzing filled polymer solutions, as most paints are [*7*].

Gas chromatography is very useful for solvent identification. Solvent retention that leads to osmotic blister formation may be demonstrated by GC analysis of the blister liquid. Because of the migration of the solvent molecules into plastics such as polyethylene, glass collection bottles will provide a more accurate system for sample transportation.

A tremendously useful system of instruments is the "hyphenated" system made up of a pyrolysis/GC/FTIR/MS. In this "instrument," which is a laboratory on a bench, paint chips can be analyzed with little or no preparation. Positive identification of generic coating and polymer types, polymer degradation studies, solvent-retention analysis after years in the field, determination of catalysis levels in oil-free polyesters from field sample chips, and numerous other tasks are very easy with the instrument [*1*].

Ion chromatography is a very useful tool for the analysis of osmotic blister liquid when the problem stems from salts under the film. Analysis of soluble salts taken from a surface is also easy to accomplish by desolution followed by ion chromatography or after evaporation onto a selected substrate such as carbon by energy dispersive X-ray.

Thermal analysis techniques such as differential scanning calorimetry and thermal gravimetric analysis (TGA) are useful in determining some physical properties of coatings. DSC has been used to monitor curing profiles of powder coatings and other thermosets for many years [*8*]. TGA systems, set up to allow a flowing gas stream to sweep the escaping molecules through a heated gas cell of an infrared spectrophotometer, are now available. This system of instruments allows studies of the thermal stability of polymers used in coatings.

Surface analysis such as X-ray photoelectron spectroscopy (XPS), auger, scanning electron microscopy (SEM), and energy dispersive X-ray (EDX) are analytical techniques that look at the surface of the coating or substrate. Auger and XPS are tremendously important in determining the locus of failure when investigating coating delamination [*6*]. A major failure mode is the development of a weak boundary layer. These are not easy to identify with the naked eye. What may appear to be an adhesive failure could be the splitting of an organic layer very near the interface due to the loss of reaction caused by a rogue metal specie. Zinc is such a culprit

when overcoated with oil-free, polyester-based systems cured by a free radical mechanism. This has been seen when a zinc-rich coating had been applied by mistake and then removed by abrasive blasting. This left trace amounts of metallic zinc alloyed into the steel surface. The zinc interfered with the curing mechanism of the polyester.

Atomic absorption (AA) spectroscopy is useful in determining the concentration of metals in coating systems. While lead, chromium, and other metals are controlled to protect workers and the environment, low concentrations of catalytic levels may be determined as well.

Ultraviolet (UV) weathering characteristics are evaluated in simulated weathering cabinets. When failures are thought to have originated from UV degradation, test regimes may be designed to evaluate the coatings using UV of different wavelengths.

Physical and application characteristics such as percent solids, viscosity, pot life, and others are usually monitored as a quality assurance/quality control QA/QC procedure during or prior to application. The requirement to monitor these variables is often included in the specification, and the values can be found on the daily reports of the inspectors.

Liquid chromatography such as gel permeation chromatography (GPC) and high-pressure liquid chromatography (HPLC) are useful in evaluating a polymer used as a binder of coatings. Failures associated with the migration of the smaller-molecular-weight fraction to an interface, causing the development of a WBL, is a typical example. QA/QC of incoming resins for use in a coating is another typical use.

X-ray diffraction (XRD) is useful in the analysis of any crystalline material. Since most pigments found in paint are mineral in nature and possess crystalline structure, they may be identified using this technique. Even when a coating system may be lacking an identifying collection of crystalline materials, the "amorphous signature" of the XRD scan has been used to provide information about unknown coating specimens.

Consider Potential Failure Modes and Test the Hypothesis

At some time after starting the investigation, a hypothesis can be drawn. A testing program incorporating it may be developed that will assist in proving or disproving the possibility of a failure mode.

Report the Findings

After a conclusion has been reached, a full report should be written. This would include all of the data gathered including pictures. The report should contain, as a minimum, the following sections: (1) Introduction; (2) Executive Summary; (3) Background Information; (4) Discussion; and (5) Conclusions. Since a primary reason for failure analysis is to prevent similar problems in the future, the report should be written with that objective in mind. It should also serve as a teaching aid to others.

CONCLUSION

Coating failure analysis will draw from a multitude of disciplines. To increase effectiveness, one must be willing to have an open mind during observation and study the basic chemistry and physics controlling the processes. Do not enter an investigation with preconceived ideas so strongly set so as to be swayed from seeing the small details that will define the actual failure mode. Do not be afraid of the "heavy" chemistry associated with the sophisticated analytical instrumentation that can give one very powerful insight into the systems.

While there are some coating mistakes that are commonly made, the reasons for coating failures appear to be limitless. Just as a good mechanic must know how an engine works to diagnose its problems, so too must the coatings failure practitioner know how paints work and the tools available for use in any required investigation. This knowledge of potential failure mechanisms can be extremely helpful to others, as well, including the owner, specifier, paint manufacturer, and applicator. By appreciating potential coating problems, an awareness of many important details is naturally obtained. Learning the complex chemistry of urethanes may be beyond the average applicator, but the knowledge that bubbles in urethanes may be the result of painting over condensed water on the surface forces an awareness that is very helpful.

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Part 15: Instrumental Analysis

Atomic Absorption, Emission, and Inductively Coupled Plasma Spectroscopy

70

by Dwight G. Weldon[1]

A PAINT, EVEN ONE AS SEEMINGLY SIMPLE as a red-lead alkyd, is actually a very complex system wherein a variety of components such as polymers that may or may not contain reactive functionality, pigments, plasticizers, additives, and solvents must interact in such a way that the dried film offers expected protection. In addition, quite often the film is expected to provide an aesthetic appeal. Because of this complexity, it not surprising that the complete chemical analysis of a coating can be a complicated and time-consuming task. Indeed, a complete analysis of all the components may require the use of several analytical techniques, many of which are discussed in this manual.

The intent of this chapter is somewhat more limited, as it pertains only to the analysis of coatings for metallic constituents and more specifically elements. Such compounds are widely used in the coating industry. Many pigments and extenders are inorganic compounds that may contain metals, and many driers, catalysts, and ultraviolet (UV) light absorbers are metal-containing compounds as, for example, cobalt naphthenate and dibutyltindilaurate. It should be pointed out that in theory inductively coupled plasma spectroscopy can be used to analyze all elements except argon. However, in actual practice, it applies to approximately 70 elements, many of which are not typically considered metallic by most paint chemists.

Classical wet chemical techniques are valuable in determining several of the above-mentioned paint-component compounds. However, a generally simpler, more efficient, and, in some cases, more sensitive way to achieve this involves the use of the related techniques of atomic absorption (AA), atomic emission (AE), and inductively coupled plasma (ICP) spectroscopy. It is the purpose of this chapter to briefly describe the underlying principles of these techniques and to discuss their usefulness within the coating industry.

ELECTROMAGNETIC RADIATION

A useful definition of spectroscopy is the study of the interaction of light, or more generally, electromagnetic radiation, with matter. Therefore, a logical starting place in the discussion of spectroscopic methods is a brief introduction into the nature of electromagnetic radiation.

Simply put, electromagnetic radiation is energy traveling through space at enormous velocities that are effectively the speed of light. The classical interpretation of this radiation ascribes to it a wave-like character with the propagation of the radiation likened to the ripples caused by tossing a pebble into a quiescent pond. However, certain electrical phenomena such as the photoelectric effect are more readily explained by the quantum mechanical interpretation of electromagnetic radiation which describes the radiation as small, discrete wave packets or bundles called "photons." These dual views of radiation as bundles and waves are complimentary and not mutually exclusive.

The classical, wave-like interpretation of electromagnetic radiation characterizes it by either the wavelength (λ) or the frequency (ν). Figure 1 is a simple representation of electromagnetic wave radiation wherein light is an oscillating vector with a wavelength, λ. From this, wavelength is defined as the length of a cycle, the distance between two successive maxima or minima, and the frequency as the number of cycles that take place per second. The relationship between wavelength and frequency is

$$\lambda = \frac{V}{\nu}$$

where V is the velocity of the wave front. In a vacuum, this velocity is equal to the speed of light, $c = 2.99 \times 10^{10}$ cm/s. Thus, for the radiation traveling in a vacuum, the equation is

$$\lambda = \frac{c}{\nu}$$

The electromagnetic spectrum is described in Fig. 2. The spectrum varies from high-frequency gamma rays, through the visible light region, all the way to low-frequency radio waves. The various regions of the spectrum have different energies, and therefore they interact differently with matter. The relationship between radiation frequency and its energy, E, that arose from quantum mechanics is given by the simple expression

$$E = h\nu$$

where h is Planck's constant, 6.624×10^{-27} erg-s. Thus, the higher the frequency or conversely the shorter the wavelength, the more energetic the radiation. As described in Fig. 2, the lower energy end of the electromagnetic spectrum involves low-energy processes such as rotation of molecules, whereas the higher-energy ultraviolet and visible light region involves higher-energy processes such as outer electron transitions. It is these transitions that form the basis of AA, AE, and ICP spectroscopy.

[1]Laboratory director, KTA-TATOR, Inc., Pittsburgh, PA 15275.

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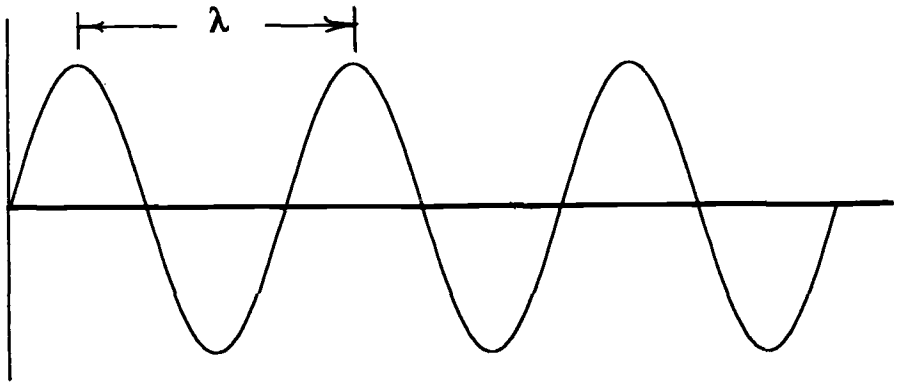

FIG. 1–Illustration of an electromagnetic wave propagating through space.

Energy, common units	100 Me V; 1 Me V; 100 ke V; 1 ke V		10^6 cm^{-1}; 25,000 cm^{-1}			33 cm^{-1}; 1 cm^{-1}		
Frequency, Hz					10^{14}	10^{12}	10^{10}	10^8
Wavelength, common units	0.1 Å; 1 Å		200 nm; 400 nm	800 nm	2.5 µm; 10 µm; 25 µm	500 µm	1 cm	1 m
Spectral region	γ Ray	X-ray	Ultraviolet	Visable	Infrared		Microwave	Radio
Optical method	γ Ray spectroscopy; Mössbauer spectroscopy	X-ray spectroscopy	Vacuum uv / Near uv; uv spectrophotometry	Colorimetry or visable spectrophotometry	Near ir / Mid ir / Far ir; ir spectrophotometry		Microwave spectroscopy; electron spin resonance spectroscopy	Nuclear magnetic resonance spectroscopy
Transition occurring	Nuclear reactions	Inner-electron transitions	Outer-electron transitions		Molecular vibrations		Rotation of molecules; spin of electrons; spin of nuclei	
Instrumentation: Source	Atomic reactor, particle accelerators	X-ray tube	Hydrogen or Xe arc	Tungsten lamp	Globar, Nernst glower		Klystron	Electronic oscillator
Instrumentation: Monochromator	Pulse-height discriminator	Crystal grating	Quartz prism grating	Glass, prism, grating, filter	Salt prisms: LiF, NaCl, KBr, CaBr		Monochromatic source	
Instrumentation: Detector	Geiger-Muller tube, scintillation counter, film		Phototube, photomultiplier	Eye, photocell, photomultiplier	Thermocouple, bolometer		Crystal diode	Diode, triode, transistor

FIG. 2–The electromagnetic spectrum and corresponding spectroscopic methods [*1*]. (Printed with permission of McGraw-Hill, Inc., from Olsen, E.D., *Modern Optical Methods of Analysis,* 1975.)

ATOMIC ABSORPTION SPECTROSCOPY (AA)

Atomic absorption spectroscopy probably is the most widely used of the three methods to be discussed. Basically, samples of coatings are chemically treated and introduced into a spectrometer that has been calibrated with known samples. For example, paint that is analyzed for lead is weighed, ashed at an elevated temperature to remove organic material, and then digested in hot nitric acid. The acid solution is diluted and fed into the spectrometer flame.

A simple, but not entirely accurate, picture of atomic structure involves negatively charged electrons rotating in orbits around a positively charged nucleus. The greatest population of atoms will reside in the lowest energy or ground state. If the atom is exposed to light of an energy exactly matching the difference between a ground-state orbital and an orbital of higher energy, a portion of this light can be absorbed and the electron can be excited such that it moves from the ground-state orbital to the higher-energy orbital. Thus, if a light source of appropriate frequency is available and is coupled with a detector capable of sensing attenuation of this light source, the concentration of a particular atomic species can be determined. This is the basis for AA spectroscopy.

Figure 3 is a simple block diagram of an AA spectrometer. It consists of an aspirator, which is used to deliver the liquid sample into a flame, and an appropriate light source that is usually a hollow cathode lamp. The cathode is made from the element of interest, encased in a glass sleeve, and maintained at a low pressure with an inert gas such as argon. The light source is positioned so that it can be focused through the flame into a monochromator (prism or grating) and onto a phototube or other suitable detector.

When an electric current is passed through the lamp, it excites the inert gas, which then impinges on the cathode and sputters off atoms of the metallic cathode material. Collisions between these neutral metal atoms and the gas ions result in promotion of the metal atoms to an excited state. When these

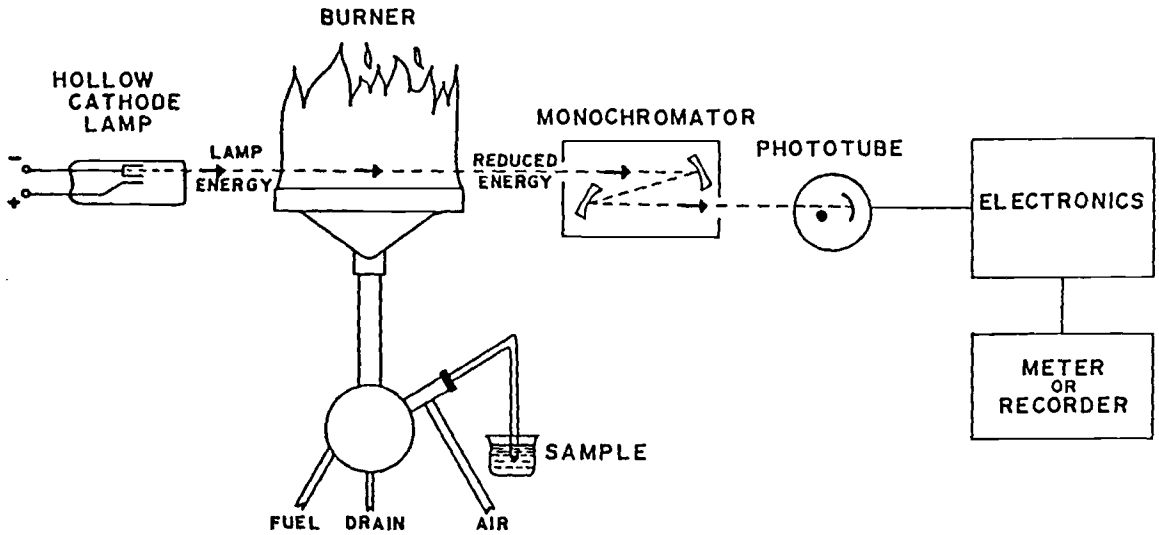

FIG. 3–Diagram of a simple atomic absorption spectrometer.

excited atoms relax back to the ground state, they emit light which is characteristic of the cathode element, and this light is then focused through the flame.

Intuitively, it would seem that there must be a relationship between the amount of light absorbed and the concentration of analyte atoms in the flame. Indeed, it has been found that if I_0 is the intensity of the incident beam originating from the source lamp and I is the intensity of the beam after it has passed through and been attenuated by the atoms in the flame of thickness or path length b, that the following relationship exists.

$$\text{Log}\,(I_0/I) = (k/2.303)b$$

where k is a constant. This relationship is known as Lambert's law. Beer found that increasing the concentration of analyte had the same effect as a proportional increase in path length. Therefore, the constant k is proportional to the concentration C of analyte and the relationship may be written as

$$\text{Log}\,(I_0/I) = abC$$

where a is the new proportionality constant. The expression is known as Beer's law.

The ratio I/I_0, which is dimensionless, is called the transmittance, T. In practical work, the terms "percent transmittance" [$\%T = (I/I_0)100$] and "absorbance" [$A = \log(I_0/I) = -\log T$] are the parameters most often used, and Beer's law is often expressed as

$$A = abC$$

Because the relationship between absorbance of an analyte and its concentration depends on the constant, a, and the path length, b, each instrument must be calibrated before a quantitative analysis can be performed. Methods of calibration are discussed in the references to this chapter and in many other analytical texts. Often calibration involves measuring the absorbance of a series of standards of known concentration and constructing a calibration cure, or the use of internal standards [*1*].

One of the inherent drawbacks to AA is the need to use a different lamp for each element to be detected, although some multi-element lamps that contain as many as five or six metals exist. Since specific cathode tubes are needed, AA is quantitative and not qualitative in nature.

Flame Characteristics

Although the processes taking place within a flame are very complex, the flame serves three basic functions:

- sample volatilization
- decomposition of molecular compounds to the elements of interest
- excitation of the individual atom (AE only)

The flame consists of three regions: an inner core, an interconal zone, and an outer cone. The analytical measurement is generally carried out in the interconal zone, which is the hottest part of the flame. The height of this zone above the burner varies with the type of gases being burned, their flow rate, and the burner type.

A very important property of the flame is its temperature, since thermal energy is responsible for decomposing samples into individual atoms and, in the case of AE, for exciting the atoms thus formed. The most common flame type is the air-acetylene flame, which achieves an interconal-zone temperature of approximately 2200°C. If a nitrous oxide-acetylene flame is used, the temperature is approximately 2900°C.

Hotter flames are usually more advantageous because they reduce the number of chemical interferences. One primary source of chemical interference is compound formation within the flame, resulting in broad-band absorption and emission. As flame temperature is increased, many of these compounds are decomposed into the free atoms and the problem is eliminated. Also, hot flames are desirable in AE since they will provide more energy for the excitation of an increased number of elements. Too high a temperature should be avoided since it is possible that a significant portion of the neutral atoms may become ionized rather than simply excited.

Graphite Furnace

A modification of AA involves the use of a graphite furnace rather than a flame to achieve excitation. Small graphite tubes or boats that have electrical contacts through which an electrical current can be passed are the basis of this technique. A small amount of sample is precisely measured into the graphite furnace, the current flow is begun, and a very high temperature is achieved, resulting in the production of an atomic vapor.

The graphite tubes are usually about 5 cm in length and about 1 cm in diameter. The sample is introduced with a micropipette through a hole in the top of the tube. The radiation from the hollow cathode lamp is focused through the axis of the tube. Heating is usually accomplished in stages. The first stage is a low-temperature step that has the purpose of volatilizing any water or solvent in the sample. The second, somewhat higher temperature, step is used to ash the sample, and this is followed by a rapid increase in current to achieve temperatures of 2000 to 3000°C and atomization of the unknown elements whose absorption is then measured.

The main advantage of the graphite furnace technique is improved detection limits due to greater sampling efficiency. Flames have low efficiency because flow down the drainage tube (see Fig. 3) results in most of the sample never getting to the flame, and also because the residence time of the atoms in the analytical portion of the flame is very brief. In contrast, graphite furnace atomizers utilize almost all of the sample and residence time is greatly increased.

Cold Vapor and Hydride Generation

Some elements, such as mercury, arsenic, tin, and antimony, are best analyzed in the vapor state. In this technique, the elements (except mercury) are converted to their gaseous hydrides with sodium borohydride in a reaction vessel. The gaseous hydrides are swept by an inert gas, such as argon, into a heated quartz cell that is located over the burner assembly area heated by the flame. A cold vapor technique is used for mercury.

An example where this technique might be useful is the case of tin. Organo-tin compounds are often used at very low levels as catalysts in certain urethane coatings. The typical detection limit for tin by conventional flame AA is 0.1 part per million (ppm), whereas the detection limit for the hydride method is 0.0002 ppm [*2*].

ATOMIC EMISSION SPECTROSCOPY (AE)

Instrumentation for atomic emission spectroscopy is very similar to that used for AA. In fact, the same instrument can usually be used for both methods. AE relies on detection of energy emitted from excited atoms as they relax to their ground state configuration as opposed to measuring the decrease in signal strength due to absorption of energy by ground state atoms being raised to an excited state. Since in AE the source of the measured light is the analyte itself, there is no need for an external light source such as the hollow cathode lamp used in AA. For this reason, the technique is more readily adaptable to multi-element analysis than AA. However, the number of elements readily analyzed by AE is considerably smaller than that detected by AA.

SOURCES OF INTERFERENCE

Spectral interference can affect AA and AE results. It can be caused by the overlapping of a line or band originating from an impurity element with the line being measured. For example, in emission analysis of sodium, the presence of calcium can give rise to spectral interference since thermally stable calcium hydroxide can form in the flame. This compound emits a band of radiation that overlaps the characteristic 590-nm line of sodium. This can be reduced to a certain degree if a monchromator of high resolution is used in AE.

Such spectral interferences are less common in AA than in AE. In AA the line source is the extremely narrow line produced by the hollow cathode lamp, and, therefore, monochromator resolution is less important in AA. However, there are still a few cases of spectral interference in AA. For example, both iron and platinum have absorption lines very near 272 nm, and manganese and gallium have lines near 403 nm.

Problems can be caused by chemical interference, which can decrease the population of free metal atoms and thereby yield an artificially low result. For example, many elements form stable oxides or hydroxides within a flame. Lithium is known to form a hydroxide in the flame. Such interferences can be minimized by increasing flame temperature.

Other types of interference include broad-band absorbance that is caused by molecules that have either formed or not been completely dissociated in the flame or by particulate matter in the flame.

Background Correction

Instrument manufacturers have devised a variety of instrumental methods for background correction. Background correction with a deuterium lamp relies on the fact that this lamp provides broadband continuous radiation in the ultraviolet region. By having a relatively wide slit width, the fraction of this radiation absorbed by the analyte is very small compared to the broadband absorbance due to molecular species in the flame or by scattering. Therefore, this type of interference can be corrected by simply subtracting the absorbance of the deuterium lamp from the absorbance of the hollow cathode lamp.

Another type of background correction utilizes the Zeeman effect. When vapor phase atoms are subjected to a strong magnetic field, a splitting of the electronic energy levels occurs. This produces, in the simplest case, three lines separated by a fraction of a nanometer and is termed the "Zeeman effect." The central, strongest line only absorbs radiation that is plane-polarized with the magnetic field, while the two weaker lines do not absorb radiation of this polarity. By mounting a rotating polarizer after the hollow cathode lamp, absorption by the analyte occurs only during the proper orientation of the polarizer. When the polarizer is in the opposite orientation, no analyte absorption occurs. Since background absorption and scattering occur during both cycles, it can now be subtracted to give only the absorbance due to the analyte.

The Smith-Hieftje technique relies on the observation that when hollow cathode lamps are briefly and cyclically pulsed at high currents, the emission band of the excited species is significantly broadened. The total absorbance from analyte plus background is obtained during the low current cycle, whereas the total absorbance during the high current pulse is primarily due to background. The signals can be subtracted from one another to obtain the corrected, analyte signal.

INDUCTIVELY COUPLED PLASMA SPECTROSCOPY (ICP)

Inductively coupled plasma spectroscopy is another technique for elemental analysis. As with conventional AE, the technique relies on measurement of light emitted when excited state atoms relax to their ground state. The major difference is that ICP accomplishes this through the use of a plasma rather than a flame. The plasma is formed as a result of argon gas being excited by an inductively coupled radio-frequency generator. One of the key elements in the instrument is the plasma torch into which the sample is carried by a rapid flow (~1 L/min) of argon.

The plasma is roughly 2 cm in diameter and is maintained within a water-cooled induction coil at the top of the torch. The torch consists of concentric quartz tubes through which argon flows. The plasma has a very intense, brilliant core. The temperatures in the plasma reach anywhere from 5000 to 7000°C, which is over twice that of most conventional flames used in AE. This higher temperature allows excitation of a greater number of elements than would be possible in a conventional flame, thereby extending the scope of the technique. Furthermore, it shares the advantage of AE over AA in that individual hollow cathode lamps are not required. Therefore, when coupled with either a rapid scanning or a multichannel monochromator, ICP is a very efficient technique for conducting simultaneous multi-element analyses.

The higher temperature of the plasma in comparison to the flames results in more complete atomization and reduction in chemical interference. Although it would seem that the higher temperature of the plasma would result in increased sample ionization and therefore poorer determination limits, this is not the case because of the suppression effect caused by the large amount of argon ions [*3*]. Detection limits are typically an order of magnitude better than AA, and the calibration curves are also linear over a much wider range.

Although the various instrument manufacturers have their own designs, there are basically two types of ICP spectrometers: sequential and simultaneous.

In most sequential spectrometers, the light dispersed by a movable diffraction grating is focused on a fixed detector, allowing emission intensities to be measured over a wide range of frequencies. Alternatively, the grating can be kept at a fixed position and the detector moved [*4*]. Since the scan speed is relatively fast and since there is no need to install and change hollow cathode lamps, the technique is much faster than AA when more than five or six elements per sample are being determined. Indeed, current instruments have throughputs ranging from 20 to 50 elemental determinations per minute [*5*].

In simultaneous spectrometers, a series or bank of detectors, such as photomultiplier types or diode arrays, are positioned at fixed points about the grating so that light at several, preselected frequencies is measured simultaneously. This is a much faster technique than the sequential method, especially if ten or more elements are being determined per sample. A disadvantage with the simultaneous instruments is their lack of flexibility. Since only a limited number of detectors can be used, only a limited number of preselected analytical lines can be measured. Typically, instruments can be set up to determine approximately 30 to 40 elements, although some can accommodate more than this.

Therefore, although able to detect more elements at somewhat better detection limits with an extended linear calibration curve compared to AA and AE, the biggest advantage of ICP spectroscopy is speed and especially so when multi-element analyses are performed. However, speed comes at a price. Conventional AA/AE spectrometers can be purchased for $15,000 to $30,000, whereas sequential ICP instruments are typically $50,000 to $75,000, and simultaneous instruments are well over $100,000. Therefore, if only a few samples are being analyzed per day for two or three elements, which is often the case in most coating laboratories, AA or AE is probably the most cost effective choice.

APPLICATIONS

Approximately 70 elements can be detected in a practical sense with either AA or AE. Detection limits are typically subpart per million. Thus, the techniques are both versatile and sensitive. Although several hours may be required for sample preparation, the actual analysis step is usually extremely rapid. Samples must be introduced into the instruments as liquids of low viscosity with the material to be analyzed in a dissolved state. Some limited work has been done on fine suspension samples.

One of the most common uses of AA spectroscopy in the coating industry is determination of lead. Lead had become a major health concern, and its presence can greatly impact the cost of removal and disposal of old paint from various structures. The commonly accepted method for lead determination is ASTM Test Method for Low Concentrations of Lead, Cadmium, and Cobalt in Paint by Atomic Absorption Spectroscopy (D 3335). In this method, the dried paint is ashed to burn off the organic materials and then digested in hot nitric acid. The method is also used to determine cadmium pigments and cobalt contained in some driers.

ASTM Test Method for Low Concentration of Mercury in Paint by Atomic Absorption Spectroscopy (D 3624) is used for the determination of mercury that is contained in many common fungicides used in paint. The sample is decomposed at elevated temperature, dissolved in sulfuric and nitric acids, diluted, and analyzed using a cold-vapor AA technique.

ASTM Test Method for Low Concentrations of Chromium in Paint by Atomic Absorption Spectroscopy (D 3718) involves ashing dried paint followed by digestion with potassium permanganate and sulfuric acid, dilution, and analysis.

ASTM Test Method for Low Concentrations of Antimony in Paint by Atomic Absorption Spectroscopy (D 3717) involves

ashing dried paint followed by refluxing with hydrochloric acid and stannous chloride.

Other ASTM atomic absorption and emission tests include:

- ASTM Test Method for Analysis of Aqueous Leachates from Nuclear Waste Materials Using Inductively Coupled Plasma-Atomic Emission Spectrometry (C 1109)
- ASTM Test Method for Determining Elements in Waste Streams by Inductively Coupled Plasma-Atomic Emission Spectrometry (C 1111)
- ASTM Test Method for Major and Minor Elements in Coal and Coke Ash by the Atomic Absorption Method (D 3682)
- ASTM Practice for Flame Atomic Absorption Analysis (E 663)
- ASTM Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (D 4951)

A method for determination of zinc in cured films of inorganic zinc-rich primes that has been used in the author's laboratory involves digestion of the sample in 1:1 hydrochloric acid:water for 20 to 30 min followed by filtration and dilution. Results in good agreement with the manufacturer's published values have been obtained for a variety of coatings.

It should be pointed out that the usefulness of AA and AE spectroscopy is not limited to published ASTM test methods. The techniques are versatile, and in-house methods can often be devised to perform a variety of analyses. An excellent source of published test methods can be found in the journal *Analytical Chemistry*, "Application Reviews," usually published in the June 15 edition of every odd-numbered year since 1987 and in the April editions prior to 1987. For instance, the 1989 review [*6*] listed ten AA and AE methods for coatings and related products. These included determination of lead content in household paints, of nickel and cobalt in coatings for brass, of sodium and silicon in surfactants, and of metallic elements in poly(vinyl chloride). The 1993 review [*7*] lists 13 AA/ICP methods.

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Chromatography

by Rolando C. Domingo[1]

CHROMATOGRAPHY IS A TERM THAT DENOTES a myriad of laboratory separation processes based on a differential migration phenomenon. It is particularly effective for the resolution of complex mixtures; hence, it can be used as a chemical preparatory method or, more importantly, as an analytical tool. This potent analytical technique has been widely used in the paint industry for a broad range of coating applications from everyday routine analysis to fundamental research into the nature of organic coating systems. Its use has been so extensive that virtually every type of material used in paint has been affected by chromatography.

Chromatography possesses certain inherent features that offer distinct advantages over conventional analytical techniques: complex mixtures, including isomers and homologs, can be separated; most of the equipment is relatively simple and inexpensive; chromatographic procedures are applicable to a broad spectrum of chemical types and are adaptable to both micro- and macro-size samples; and chromatography is capable of both qualitative and quantitative functions even when applied to multicomponent systems.

The term *chromatography* was coined by Tswett [*1*] who, in 1906, used powdered chalk and petroleum ether to separate plant pigments into colored zones of isolated pigment. As early as 1930 the technique was applied successfully to colorless materials, but the name remained unchanged. The term is currently used to signify a broad group of separation techniques, most of which are independent of color.

GENERAL PRINCIPLES

Considered simply, the chromatographic process involves the differential migration of sample components as they are moved through a chromatographic system. The rates of migration for various components are related to their unequal distribution between two phases, a moving phase and a stationary phase. Distributions are determined by driving and resisting forces that are exerted between the two phases and the components in the sample. These forces are influenced by the chemical structure and the size and shape of molecules present in the chromatographic system and in the sample. Generally, the stationary phase is a finely divided solid serving as an adsorbing surface or a liquid supported by some inactive porous media; the mobile phase is usually liquid or gas. The effectiveness of a chromatographic separation depends upon proper selection of phases, and, although the choice is often made on an empirical basis with heavy reliance on experience, the best results are obtained by the application of established theoretical principles. Phases are selected so as to take advantage of some functional incremental differences in the properties of the compounds to be separated; for the most part, these are differences in molecular size, solubility in the liquid phase, and adsorption to the solid phase. In today's capillary gas chromatographic columns, solid supports are no longer used. Instead, the liquid or stationary phase is coated onto the wall of the capillary tubing. To improve thermal stability, the stationary phases are oftentimes chemically bonded to the tubing wall.

In practice, there are certain basic fundamentals that apply to all differential migration techniques, regardless of the separation media used: flow rates must be slow enough to allow equilibrium to occur between phases; solute concentration must not exceed the adsorption capacity of the stationary phase; and the greater the difference in partition ratio between phases, the shorter the migration path required for resolution. Since the efficiency of all chromatographic processes is governed by the above factors, these concepts should be kept in mind when a system to be used for a given separation is being considered.

Chromatographic separations are conducted usually in columns of carefully graded sorptive powders, in sheets or strips of porous media such as paper, or in thin layers of powdered adsorbents spread on rigid surfaces. After a suitable system has been selected, a small quantity of the mixture is placed at one end of the chromatographic column and transported through the stationary phase with solvent or gas. Isolated compounds are detected "on column" if they are visible or "off column" by chemical or electronic means after leaving the column. A permanent record of the separation may be obtained by photographing the column, by plotting some property of the separated components against elution volume on graph paper, or by electronic recording. Such records are referred to as *chromatograms.*

GENERAL METHODS

Frontal, displacement, and elution analysis are the three basic methods for conducting chromatographic separations, and each has its own unique function. Separations are determined by adsorption or partition interplay between sample, stationary phase, and moving phase.

[1]DSM Desotech Incorporated, 1122 St. Charles Street, Elgin, IL 60120.

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Frontal Analysis

Frontal analysis separations are made by the continuous addition of the sample onto a column containing an adsorbent. As the sample passes through the column, the component having the lowest adsorption affinity for the adsorbent emerges first. After the most strongly adsorbed component has saturated the column, the sample flows through the column unchanged. Only a limited portion of the least adsorbed component can be obtained in pure form. Frontal analysis is not an effective method for resolving mixtures, but it does provide a means of treating solutes having strong adsorption characteristics. This means of separation is seldom used in the coatings industry because of the advances in column technology for both liquid and gas chromatography.

Displacement Analysis

In this method, a concentrated portion of a sample is adsorbed onto a column, followed by the addition of a solvent (developer) that is adsorbed more strongly than any of the components in the sample. As the developer passes through the column, the components are displaced and forced ahead of it. Components will also displace one another so that the one least strongly adsorbed emerges from the column first, followed by the others in the order of increasing adsorption affinity. The component with the greatest adsorption affinity elutes last, immediately ahead of the displacing solvent. Under optimum conditions, each component will move through the column as a "belt" of pure material. A graph, obtained by plotting volume against some physical property of the effluent, will contain a series of steps. Under standardized conditions, the height of each step is used for identification, and the length of each plateau is used to determine relative amounts. When put to practice, all reversibly adsorbed components are moved through the column, but they are not resolved completely. The trailing edge of one component will overlap the leading edge of the following component, and, although it is not possible to completely separate each component in its pure form, normally a relatively pure fraction of each is attainable.

Elution Analysis

Elution processes are conducted by introducing a concentrate of the sample onto a column followed by the addition of an unadsorbed moving phase. As the sample mixture is washed through the column, components are selectively retarded and separated into discrete zones that are isolated by the presence of the moving phase between zones. This procedure contrasts with displacement and frontal methods by having the eluting solvent pass through the sample. Theoretically, complex mixtures can be completely resolved; hence, elution chromatography has the potential of being a good procedure for qualitative and quantitative analysis.

Of the three processes discussed, elution chromatography is the most efficient method for resolving mixtures, which accounts for its being the most widely used form of chromatography.

Adsorption Chromatography

Chromatography can be further classified as adsorption and partition chromatography. In adsorption chromatography, the stationary phase is a solid, most often a powder or granular adsorbent, and the mobile phase is either a liquid or gas. Sample components are separated according to their relative adsorption on active surfaces as they are percolated through an adsorbent bed. For any particular component, the degree of adsorption is related to the competitive attraction exhibited by the adsorbent and developing phase. Thus, if a component is attracted strongly by an adsorbent and attracted weakly by the moving phase, it shows little or no movement through the column. Conversely, if it shows a greater affinity for the moving phase than for the adsorbent, it will tend to move along with the moving phase. Hydrogen bonding, dielectric constants, and dipole moment of the sample and the two phases are factors that greatly influence adsorption separations. In general, strong adsorption is favored by the presence of highly polar compounds in weakly polar moving phases.

Liquid-solid chromatography (LSC) denotes the use of a liquid moving phase, whereas gas-solid chromatography (GSC) indicates a gaseous moving phase. Prior to the introduction of partition chromatography by Martin and Synge in 1941 [*2*], adsorption chromatography was used exclusively.

A vast selection of adsorbents and mobile phases are available, providing a great deal of flexibility for separating mixtures. Various aspects of adsorption chromatography, including technique and equipment, will be discussed in greater detail during the treatment of specific methods such as "classical column chromatography," thin layer chromatography, etc.

Partition Chromatography

Partition chromatography is distinguished from adsorption chromatography by the presence of a liquid that is positioned in the system by sorption to an inactive solid support. The liquid layer is the stationary phase, and the solid merely serves as a support. Separation of compounds is related to their differential solubility in two immiscible phases. Hence, a compound demonstrating a solubility preference for the stationary liquid phase will have its passage through the column retarded. Those that are less soluble in the stationary liquid phase, but readily soluble in the mobile phase, tend to move unimpeded through the column. In a static experiment with a given set of phases, a compound will be distributed between phases in a characteristic manner. This property is referred to as its partition coefficient, k, and may be defined as follows:

$$k = \frac{\left[\begin{array}{c}\text{concentration of compound in}\\ \text{stationary liquid phase (g/mL)}\end{array}\right]}{\left[\begin{array}{c}\text{concentration of compound in}\\ \text{moving phase (g/mL)}\end{array}\right]}$$

Since components are separated by virtue of differences in their partition coefficients, conditions of a test are adjusted so as to take advantage of some peculiar to each component that magnifies quality differences in k values. Fortunately, only slight differences are required for separation, and such differ-

ences can be achieved by proper selection of stationary liquid phase.

Although partition chromatography is historically more recent, it has surpassed adsorption chromatography as a method for separating complex mixtures. In partition chromatography there is a more rational relationship between the chemical character of materials and their chromatographic behavior, which accounts for its effectiveness when applied to the separation of closely related compounds such as isomers and members of a homologous series. Adsorption chromatography, however, is more limited in its applications; it will distinguish between classes of compounds, but there is little subfractionation within classes.

LIQUID CHROMATOGRAPHY

Of the various forms of chromatography, the form using a liquid eluent came first. Liquid chromatography (LC) is characterized by the employment of a liquid moving phase; the stationary phase may be either liquid or solid. The separation of molecules is based on their preference for a liquid or solid stationary phase relative to a liquid moving phase. LC encompasses established techniques such as paper, thin layer, "classical column," and gel permeation chromatography, all of which have been used extensively for routine and research purposes. For the purpose of clarity and continuity, the different chromatographic techniques will be discussed as separate entities, but, in some cases, there has been a fusion of techniques. For instance, papers have been impregnated with ion exchange materials; gels, the material commonly associated with gel permeation chromatography, have been spread on thin plates for thin-layer separations.

"Classical Column" Chromatography

The term "classical column" chromatography is used here to define procedures usually associated with older forms of chromatography. The method involves the introduction of a sample onto a column packed with adsorbent; separations are facilitated by the addition of a displacing or eluting solvent.

Apparatus and Technique—The essential equipment consists of container, adsorbent, and developing solvent. The container for the column of adsorbent is usually a glass tube, from about 5 to 50 mm in internal diameter, with a working height of from 5 to 25 times the diameter. Columns prepared from plastic and metal tubes have been also used. Fritted glass disk, perforated plastic, cotton, or glass wool may be used at the base of the column to support adsorbents such as silica, magnesium and aluminum oxides, calcium phosphate, charcoal, and cellulose. Adsorbents vary in their capacity and activity, with activity increasing with decreasing particle size and water content. If practical flow rates are to be realized, it is necessary to use relatively large particles, but not so large as to reduce the capacity below reasonable limits. In addition, narrow mesh ranges provide more uniformly packed columns and columns of higher efficiency. Adsorbents may be packed in two ways, as a dry powder or as a slurry. To ensure uniformity, the tube should be vibrated frequently and a vacuum or pressure applied during addition of packing material.

Although the activity and capacity of different adsorbents are not the same, the sequence of eluting power for different solvents is the same for any given adsorbent. In order for separation to occur, the eluting solvent must be appropriate to the packing material and sample. For example, a very polar solvent will displace the sample completely with little or no separation of components; on the other hand, a very nonpolar solvent may cause all of the components to adsorb on one section of the column with little migration or separation of components. A general practice is to start the analysis with the most nonpolar solvent and gradually change to solvents of increasing polarity. The process of systematically changing the composition of eluting media during a chromatographic analysis is referred to as gradient elution [2]. Strain [3,4] lists absorbents according to their absorptive strength and solvents in the order of their eluting power.

An analysis is conducted by introducing a sample in a few milliliters of nonpolar solvent and allowing it to flow onto the column. The eluting solvent is added, in small increments at first, and then in large quantities. At no time during the analysis is air drawn through the column. If colored compounds are chromatographed, they are detected visually on the column or in the effluent. Certain colorless compounds may be examined by fluorescence when exposed to ultraviolet radiation, or the packing may be extruded and the components detected after treatment with reagents. Eluted components are identified by dividing the effluent into aliquots and determining such properties as refractive index, nonvolatile content, pH, optical density, etc. Automatic fraction collectors, actuated by weight of fraction or a timing device, can be used to avoid manual collection of effluent.

Classical chromatography, as it is commonly used, is relatively simple but lacks detector sensitivity and is time consuming. The latter is particularly true when a fresh column is required for each analysis. Nevertheless, this type of chromatography has contributed to the general knowledge of organic coatings and to paint analysis.

Applications—ASTM Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption (D 1319) describes the determination of hydrocarbon types in petroleum products. A column is packed with activated silica gel containing a mixture of fluorescent dyes. A hydrocarbon mixture is introduced onto the gel, and isopropyl alcohol is added to desorb the sample down the column. The hydrocarbons are separated according to their adsorption affinities; aromatics are retained the most tenaciously, immediately followed by olefins, and finally by saturated hydrocarbons. The fluorescent dyes are also separated selectively with the hydrocarbon types and make the boundaries of the aromatic olefin and saturate zones visible under ultraviolet radiation. The volume percent of each type of hydrocarbon is calculated from the length of each zone. A separation of this type is an example of adsorption chromatography by displacement; the developing solvent in this case is isopropyl alcohol. Hydrocarbon types in mineral spirits and VM&P naphtha have been determined using this method.

Loeblich and Lawrence [5] used partition chromatography for the qualitative and quantitative analysis of rosin and modified rosin products. The column is packed with 2-aminopyridine-furfuryl alcohol on silicic acid. The alcohol serves as the stationary liquid phase; isooctane is the eluting solvent.

Fractions are collected and titrated with 0.01 *N* sodium hydroxide solution.

Swann et al. [*6*] used carbon black and asbestos to separate phthalate plasticizers from phthalate resins. Phthalate resins were retained selectively on the column, and phthalate plasticizers were detected and measured by saponification of the effluent.

HIGH PRESSURE LIQUID CHROMATOGRAPHY

In recent years the term liquid chromatography has acquired new significance by being used to denote a completely integrated column-detector-recorder system. New developments in instrumentation make use of the principles and practices commonly associated with gas chromatography, the object being the attainment of rapid and high-efficiency separations. Traditional methods, out of necessity, employ large samples, slow flow rates, and short columns, conditions that are not conducive to rapid, efficient analysis. With the advent of high-pressure flow systems and highly sensitive continuous flow detectors, operating conditions closely approaching those used in gas chromatography may now be used. The total unit consists of thermostated columns, solvent reservoir, degasser, metering pump, detector, and strip-chart recorder/electronic integrator.

The resurgent interest in liquid chromatography has prompted an ever-increasing number of instrument manufacturers to produce highly sophisticated instruments that are capable of multiple modes of operation including adsorption, partition, and gel permeation separations. The term *high pressure liquid chromatography* (HPLC) will be used in this section to designate adsorption and partition separations based on advanced liquid chromatography technology. Descriptions of liquid chromatographs have been presented by Lambert [*7*], Stouffer et al. [*8*], and Jentoft and Gouw [*9*], the principal differences being in the techniques used to monitor the sample stream.

HPLC has already reached the level of acceptance enjoyed by many other chromatographic techniques. Its potential as an analytical tool is still creating an enormous amount of interest. In the past, most publications were concerned with the refinement of instruments with less emphasis on applications. Presently, publications are now focusing on the applications of HPLC in the paint and coatings industry. HPLC complements other forms of chromatography. For example, HPLC can be used for the analysis of compounds having a broad range of molecular weight, whereas thin-layer and paper chromatography are limited to nonvolatile compounds and GC is limited to those that can be vaporized. HPLC is usually regarded as a relatively slow method when compared to other chromatographic techniques. However, the time necessary to produce a separation is related directly to the resolution required. HPLC can make separations of simple mixtures at speeds comparable with GC; complex samples may still require several hours. Readers are encouraged to read ASTM Practice for Liquid Chromatography Terms and Relationships (E 682-79).

Apparatus and Technique—Figure 1 shows the pertinent components of a liquid chromatograph. Solvent from one of the reservoirs is moved through a degasser by a pulse-free pump that is capable of delivering flow over a wide range of pressures. The flow is split into two streams; one is directed to the reference side of a differential detector, the other is allowed to pass through a sample injector, fractionating column, and finally to the sample side of the same detector. The sample is introduced with a syringe, or sample loop, located at the entrance to the column, and the effluent from the column is generally monitored by a continuous flow differential detector.

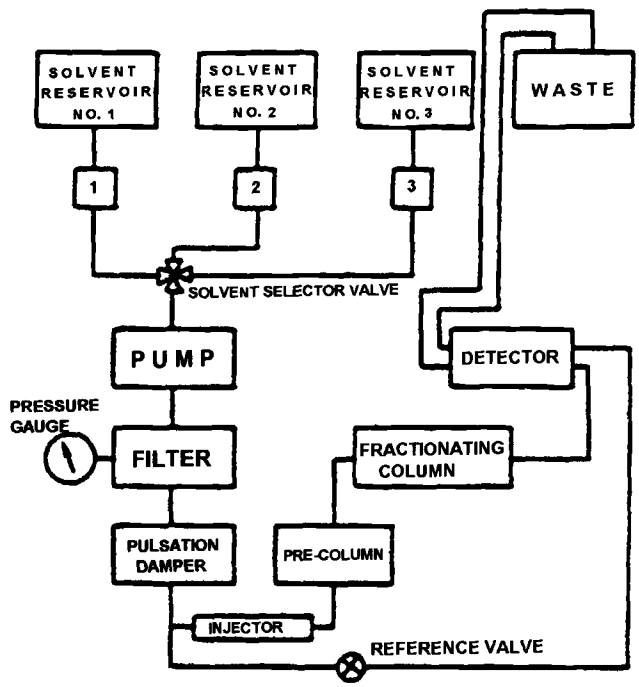

FIG. 1–Schematic diagram of a high-pressure liquid chromatograph.

Most column packings used in traditional methods for both adsorption and partition separations may be used for HPLC, for example, silica gel, alumina, diatomaceous earth, etc. There have been, however, newly developed packings that greatly extend and enhance the use of HPLC.

In the past, the development of LC was impeded by hydraulic difficulties and detector problems, but with the advent of improved solvent transport equipment and high-performance continuous flow detectors, HPLC has been elevated to a position of new prominence. At this point, it is needless to belabor the importance of each of these two factors. However, the performance characteristics of the various detectors should be carefully considered since the type used directly influences the effectiveness of the total system. Some detectors are selective, responding to only certain classes of compounds, while others are applicable to a wide range of classes and have broader application. For this reason best use is made of detectors in the context of the complete system and sample to be analyzed. Photometric, refractometric, calorimetric, radiometric, polarographic, and ionization detectors have been evaluated by Huber [*10*]. He concluded that all of them can be used for HPLC, but that a universal, all-purpose detector is not yet available. Some of the more conspicuous detectors will be discussed briefly so as to provide background regarding principle of operation and area of usefulness.

At the present time, refractive index comes closest to being the universal detector for liquid chromatography. Detection depends on the difference in the refractive indexes of pure solvent flowing through the reference side of the detector and of the effluent from the analytical column; measurement is nondestructive to the sample, the level of sensitivity is good, and operation is simple. Use of the refractive index detector in liquid chromatography is discussed in ASTM Practice for Refractive Index Detectors Used in Liquid Chromatography (E 1303-89). As with other nondestructive detectors, when used in conjunction with an automated fraction collector, the sample can be isolated and subjected to further treatment.

The heat of adsorption detector is also applicable to a wide range of materials since it responds to an almost universal property of materials, heat of adsorption. Thermal changes, induced by the adsorption and desorption of the sample, are sensed, amplified, and recorded as positive and negative peaks on a chromatogram.

The flame ionization detector, also called chain, cord, and belt detectors, combines high sensitivity and quantitative analysis with wide dynamic range. In flame ionization detection, all of the carrier leaving the column can not be directed through the detector; instead, a small wire or belt is passed continuously through the eluting stream collecting a portion of the sample. The carrier solvent is flash evaporated in one chamber, and the sample residue is then moved into a pyrolysis zone where the sample is decomposed thermally and detected with a flame ionization detector. Since the carrier solvent is removed completely, this type of detector is not affected by gradient analysis, but at the same time, its use is restricted to nonvolatile compounds. Obviously, this type of detector is well suited for the analysis of resins, polymers, and oils.

Photometric detectors measure the difference in ultraviolet light adsorption between a sample and reference stream. Since ultraviolet adsorption is parameter-specific, this type of detector is limited to chromophores. This property, of course, can be advantageous when nonultraviolet and ultraviolet adsorbing compounds emerge from a fractionating column together.

Applications—Bombaugh et al. [*11*] were able to separate ethylene glycol, diethylene glycol, and triethylene glycol using a column packed with porous silica beads; the eluting solvent was water in methyl ethyl ketone, and the eluted compounds were detected using a differential refractive index detector. Poulson and Jensen [*12*] used an adsorption column composed of 100 to 200-mesh silica gel for the separation of alkene-alkane hydrocarbons. Diatomaceous earth coated with various liquids was used to separate and determine aromatic hydrocarbons [*13*]. The compounds were sensed with a differential photometric detector. ASTM Practice for Testing Fixed-Wavelength Photometric Detectors Used in Liquid Chromatography (E 685-79) discussed the use of the fixed wavelength photometric detectors in liquid chromatography.

PAPER CHROMATOGRAPHY

Paper chromatography, as the name implies, uses paper as the separation media. A strip of filter paper is spotted with the sample near one edge and is arranged so that developing solvent can move by capillary action through the sample. The differential distribution of components between phases (paper and developing solvent) causes them to migrate at characteristic rates. If compounds are colorless, reagents may be applied to reveal them as circular or elliptical spots.

The popularity of paper chromatography can be attributed to several desirable qualities. The method is extremely versatile and simple, it allows for simultaneous analysis of several samples on one paper, and optimization of the developing solvent is easily controlled. On the other hand, one should be cognizant of certain disadvantages. The sample must be nonvolatile or be capable of conversion to a nonvolatile derivative before analysis, the length of the migration path is limited, and quantitative analysis is moderate. Most important, extraordinary precautions must be taken to reproduce conditions of test in order for retention data to be reproducible and significant.

Apparatus and Technique—The equipment necessary to conduct paper chromatography involves materials common to most laboratories. Whatman No. 1 filter paper has been the type most widely used, but for many analyses, other types of filter papers are adequate and sometimes preferred. A large assortment of containers has been employed as developing chambers: glass jars, test tubes, graduated cylinders, specimen tanks, and pipes can all be used if they are provided with tight-fitting lids. An unlimited number of liquid mobile phases are available; the type used is dictated normally by the polarity of the sample.

Capillary action is the principal dynamic force involved in ascending, lateral, or radial paper chromatography. However, in the case of descending chromatography, the movement of solvent is initiated by capillary action and finished by gravity. Occasionally, particularly when complex mixtures are encountered, it may be necessary to employ a two-dimensional technique. In this type of analysis the separation is carried out using one solvent in one direction, drying the sheets, and finishing the separation at right angles with another solvent. In all paper chromatographic separations, it is essential that the internal volume of the developing chamber be saturated with vapors from the eluting solvent.

If cellulose papers are exposed to water vapor, they will adsorb about 22% of water that may serve as the immobile liquid phase for reverse phase chromatography. Where water is impractical as an immobile phase because of sample insolubility, papers can be impregnated with other liquids such as kerosene, silicone oil, and olive oil. It is sometimes necessary, for the solution of special problems, to alter the composition of the paper. This can be done by direct chemical treatment or by the addition of a material having special properties, such as an ion exchanger. Papers of this type represent a departure from conventional paper chromatography since principles based on other techniques are involved.

Under stringently controlled conditions, compounds may be identified by their R_f values. The R_f value is the ratio of distances traveled by a compound and the solvent front, expressed as follows:

$$R_f = \frac{\text{distance moved by compound}}{\text{distance moved by solvent front}}$$

Although the use of R_f values is well documented in the literature, they are often difficult to reproduce and should be used with caution. When R_f values are reported, detailed in-

formation concerning all of the operating parameters must be stated.

Since it is possible to conduct multiple analyses on one sheet, an unknown mixture can be identified by analyzing it in parallel with standard compounds; direct comparison can be made with respect to the retention characteristics of both the sample and standard. If standards of known concentration are run simultaneously with the unknown, the amounts of each isolated component can be estimated from their relative intensities.

For additional information regarding the theory and practice of paper chromatography, the reader is referred to books by Hais and Macek [*14*] and Block et al. [*15*].

Applications—Dicarboxylic acids and polyols have been identified in polyesters [*16*] by paper chromatography. Following dissolution of the resin with alcoholic potassium hydroxide, isolated dipotassium salts were converted to their corresponding acids and separation was accomplished by ascending technique. Polyols recovered from the saponification filtrate were separated by a two-dimensional technique; chloroform-ethanol mixture, used first in one direction, was followed by elution at right angle with ether saturated with water. Dicarboxylic acids were visualized with bromcresol purple, and polyols were detected by spraying with ammoniacal silver nitrate. Tawn and May [*17*] identified dicarboxylic acids and polyols in alkyd resins using a similar procedure.

Mills and Werner [*18*] identified various types of natural resins using reverse phase chromatography. Papers were wet with kerosene and were blotted to remove excess kerosene. Samples were chromatographed with a liquid moving phase consisting of isopropanol-water-kerosene. The papers were dried, sprayed with a carbon tetrachloride solution of phenol, and exposed to bromine vapor. Colors varied according to the type and amount of resin.

THIN-LAYER CHROMATOGRAPHY

In thin-layer chromatography (TLC) an aqueous slurry of a finely divided adsorbent mixed with a binder is spread on a glass plate so that a uniform, coherent film adheres to the glass. Coated plates are dried and activated by baking in an oven for a prescribed length of time. An analysis is conducted in much the same manner as in paper chromatography. A plate is spotted with a sample and placed in a chamber containing solvent. After the developing solvent has irrigated the TLC plate, the plate is removed from the tank, dried, and compounds are detected with appropriate reagents. As in paper chromatography, the vital driving force exhibited by the mobile phase is that supplied by capillary action; separation is due to adsorption or partition processes.

Paper chromatography and TLC are similar, and both share some of the same advantages such as high sensitivity, selectivity, and low cost. TLC, however, provides sharper zone separation and increased speed, 20 or 30 min for most TLC analyses as opposed to several hours for paper chromatography. TLC is subject to most of the disadvantages described for paper chromatography, for example, compounds must be nonvolatile, have a limited elution path, etc.

Apparatus and Technique—Equipment requirements for TLC are minimal. The basic materials, as shown in Fig. 2, consist of a tank, plate, adsorbent, visualization reagent, rack, and adsorbent applicator. Relatively inexpensive equipment can be purchased from distributors of chromatographic supplies; if necessary, however, apparatus can be usually improvised from material found in most laboratories.

A developing tank must have a tight-fitting lid, and it should be large enough to receive 2 by 8-in. (5.08 by 20.32 cm) or 8 by 8-in. (20.32 by 20.32 cm) plates, but not so large as to require a large solvent reservoir. A "tankless" system can be arranged by sandwiching the thin layer between two plates and placing the sandwiched layer in a shallow trough containing solvent.

The nature of the adsorbent plays a major role in determining the type of separation that will be obtained. In a broad sense, any of the adsorbents used in column chromatography can be used to prepare thin films provided they are available as powders of uniform particle size. Silica gel and aluminum oxide are used most frequently. The homogeneity and quality of adsorbent powders are important factors to be considered if well-defined results are to be obtained.

For a given adsorbent, the migration of components in a mixture is determined by the choice of mobile liquid phase;

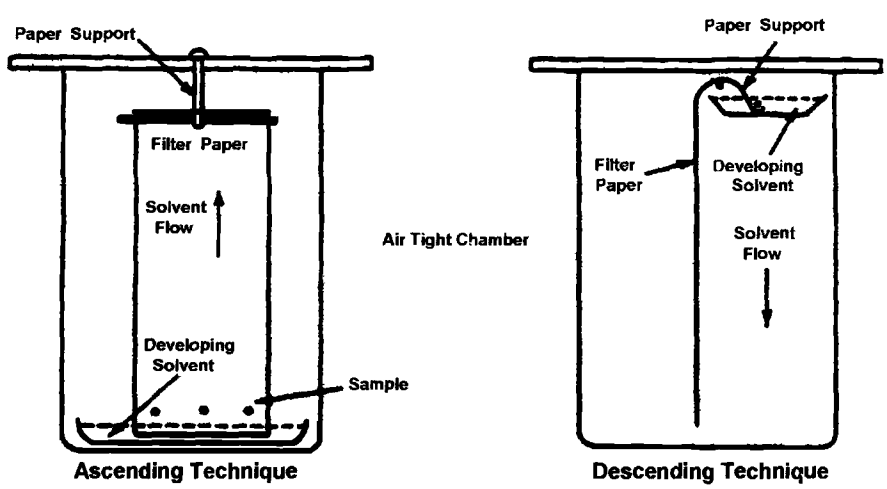

FIG. 2–Apparatus for paper chromatography.

its polarity can be altered to enhance or suppress the movement of the components. For example, if a sample moves with the solvent front, the polarity of the mobile phase should be reduced by choosing a solvent of lower polarity or by mixing solvents of different polarity. Conversely, if a sample shows little tendency to move, the polarity of the eluting solvent is increased by selecting a solvent occurring lower in the eluotropic series or by changing the ratio of polar and nonpolar solvents, favoring the polar solvent. The eluotropic series, solvents arranged in order of polarity, and other solvent activity have been described in books [*19,20*].

The preparation of chromatoplates is relatively easy and can be accomplished by using several techniques: pouring, dipping, spreading, or spraying. The first two methods require no special equipment, but they lack the refinement needed to provide uniform films. The spray technique is messy and does not always yield films of uniform thickness. By far the most popular technique is that which uses a draw bar.

Films are prepared by mixing adsorbent, binder, and water until a homogeneous slurry is obtained. Glass plates, usually 2 by 8-in. (5.08 by 20.32 cm) or 8 by 8-in. (20.32 by 20.32 cm), are aligned on a perfectly flat surface. A spreader is positioned on the end plate, charged with the slurry, and drawn across the plates with constant pressure and speed. For analytical purposes, film thickness should be in the range of 0.2 to 0.5 mm. Chromatoplates are air dried and, if desired, activated by heating at elevated temperatures. Although glass is the most common substrate, plastic and fiber glass sheets have been used successfully. TLC sheets from plastic and fiber glass can be cut and shaped with scissors. Precoated glass plates and plastic sheets can be purchased from several commercial sources, and, although the price per plate is increased substantially, the cost is still within the budget of most laboratories.

A solution of the sample may be transferred to the chromatoplate with a micropipette or syringe. After the diluting solvent has evaporated, the plate is transferred to a developing chamber where it is irrigated with the developer solvent. If a two-dimensional technique is necessary, the plate is turned 90° and treated with another solvent. The plates are dried and then sprayed with an appropriate visualization reagent.

Methods of identification are similar to paper chromatography; R_f values or "parallel analysis" are standard techniques for TLC. Additional information may be obtained by removing spots with a spatula and subjecting them to chemical or instrumental analysis.

Visual comparison with standards of known concentrations run simultaneously is often sufficient for estimating the amount of a component. If more precise quantitative information is required, instrumental methods are used. Densitometric techniques measure the density of color or acid char on the plate and relate this property to the amount of sample present. With all quantitative TLC procedures, it is important to rigidly control sample application, adsorbent quantity, and solvent composition. For an in-depth treatment of TLC theory and practice, the reader is referred to books by Truter [*19*], Bobbitt [*20*], Randerath [*21*], and Stahl [*22*].

Applications—The utilization of TLC for paint research and routine applications has been ably illustrated by Privett and Blank [*23*] and Rybicka [*24*]. The former dwells on the many general applications to fats and oils that are important to the paint chemist. For example, Fig. 3 shows the separation of various oils on a 20 by 20-cm plate coated with silicic acid (250 mils) using petroleum ether containing 15% diethyl

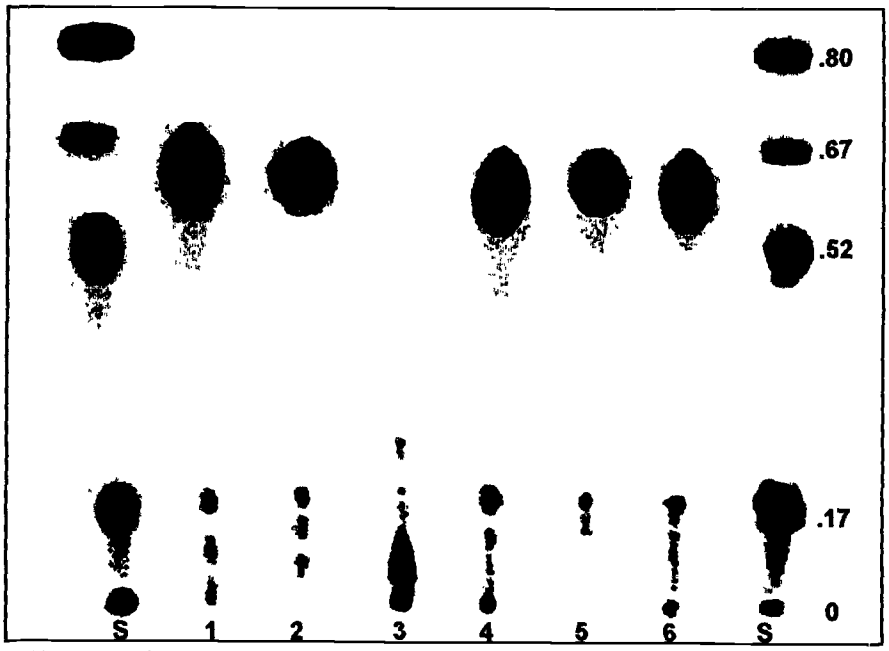

FIG. 3–TLC analysis of oils on silicic acid with 15% diethyl ether in petroleum ether containing 1% glacial acetic acid. (Courtesy of *Official Digest.*) S—Hormel Institute standards: lecithin (R_f = 0), cholesterol (R_f = 0.17), oleic acid (R_f = 0.52), triolein (R_f = 0.67), cholesteryl oleate (R_f = 0.80). 1—linseed oil, 2—safflower seed oil, 3—castor oil, 4—tuna oil, 5—olive oil, and 6—menhaden oil.

ether and 1% glacial acetic acid as the developing solvent. Zones were made visible by treating the chromatoplate with a solution of sulfuric acid and potassium dichromate. Privett and Blank also demonstrated the use of TLC for the determination of total saturated fatty acids in oils, and an investigation of a more basic nature illustrated the usefulness of thin films for elucidating mechanisms involved in the auto-oxidation of oils.

An interesting application, as described by Rybicka, illustrates the utility of TLC for monitoring glycerolysis reactions. Periodic sampling and TLC analysis on silicic-acid-coated plates were used to show how triglyceride content is decreased, accompanied by an increase in mono- and diglycerides. Similar studies with other polyols and oils were described.

A very comprehensive survey of TLC methods as applied to lipids has been made by Mangold [*25*]. Included are details for the separation of glycerides, fatty acids as methyl esters, and cis- and transisomers along with other facets of lipid analysis. Many of the methods are capable of yielding information relevant to the analysis of organic coating materials.

Knappe [*26*] demonstrated the application of TLC to a broad spectrum of coating materials including polyols, dicarboxylic acids, fatty acids, and hydrolysis products from nitrogen resins. Numerous chromatograms and comprehensive retention data were presented to illustrate applications.

Techniques for the fractionation of materials used by the plastic industry, but of importance to the paint chemist, have been described [*27–29*]. These data include tables of R_f values of polyhydric alcohols, dicarboxylic acids, and plasticizers. An impressive list of 40 plasticizers is presented in Ref *29*. Separations were performed on silica gel layers using methylene chloride as the mobile phase. Antimony pentachloride was the primary visualizing agent.

Potentially, TLC promises to be an extremely valuable tool for research and quality control problems, and wider acceptance by the paint industry should be seen in the near future. The commercialization of precoated TLC plates from several manufacturers should alleviate some of reproducibility problems associated with "home-made" TLC plates prepared in the past. Used to its fullest potential, TLC techniques can be used to screen and/or separate a wide variety of relatively nonvolatile materials prior to HPLC analyses.

GAS CHROMATOGRAPHY

Of the various forms of chromatography, that using a gaseous moving phase has proved to be the most effective for the analysis of organic coating materials. As in most chromatographic processes, the separation of compounds may occur by partition or adsorption activity—GLC and GSC, respectively. The equipment for, and the execution of, both forms are similar; however, due to its versatility and effectiveness, GLC has made a much greater impact on paint analysis, and for that reason it will be emphasized and discussed at considerably greater length. A glossary of GC terms can be found at the end of this chapter.

The primary object of this discussion is to impart to the reader a basic concept of GC processes and to focus attention on the many applications to paint analysis. Within the scope of the discussion, it will be only possible to etch the surface of present GC knowledge. If the references appear to be numerous, it is because the technique has such broad application and not because it has been exhaustively investigated.

GC is a separation technique that uses a gaseous moving phase to transport volatilized components of a sample through a small diameter tube containing a solid adsorbent or a liquid fixed to an inert porous solid. As the components advance through the column, they are retarded selectively by sequential adsorption on a solid stationary phase or by solubilization in a liquid stationary phase. A sensing device, located at the exit of the column, detects the various components by responding electronically to some physical or chemical property. From the time of appearance and the magnitude of the signal furnished by the detector, information regarding the number, type, and concentration of components can be usually ascertained.

Since the advent of GC, many time consuming and laborious test procedures have been reduced to routine methods of short duration. In addition, the unique responsive capability of GC permits the accumulation of analytical information, much of which can not be obtained by conventional techniques. In short, GC is characterized by versatility, reliability, and speed.

The outstanding popularity and performance of GC can be attributed to features that are inherent in this type of analysis. Any material that is volatile or can be converted to a volatile derivative will respond to GC. GC is extremely sensitive—as little as one nanogram of some materials can be detected. Rapid and efficient analysis is made possible by the low density and viscosity of carrier gases, which permits rapid mass transfer between phases, thereby allowing rapid flow rates. Columns can be used repeatedly; several hundred analyses on one column are not unusual. The production and interpretation of data are relatively uninvolved. On the other hand, GC has certain disadvantages. Materials remaining on a column are not detected. Owing to the empirical nature of the technique, chemical or instrumental confirmatory tests may be necessary to verify the presence of a compound, particularly when background information concerning the sample is lacking.

Ever since its introduction by James and Martin [*30*] in 1952, a wealth of GC information has appeared in the literature that has swelled to mammoth proportions. The retrieval of such information is readily made possible through the use of compiled classified indices such as bibliographies [*31,32*] and annual volumes of *Gas Chromatography Abstracts* [*33,34*]. In addition, for current developments, Preston Technical Abstract Company [*35*] offers a weekly abstract service consisting of titles of papers and abstracts. Reviews [*36–41,44,46*] reflecting specific application to organic coatings have been also published. ASTM Committee E-19 on Chromatography's *Chromatographic data compilations* [*49,50*] are arranged according to compound and liquid phase; data include relative indices for a vast number of compounds obtained on different columns. Committee E-19 has been also responsible for the publication of two general methods, ASTM Practice for Packed Column Gas Chromatography (E 260) and ASTM Practice for Gas Chromatography Terms and Relationships (E 355). ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications also pub-

also published Practice for Direct Injection of Solvent-Reducible Paints Into a Gas Chromatograph for Solvent Analysis (D 3271-87) and ASTM Test Method for Analysis of Dichloromethane and 1,1,1-Trichloromethane in Paints and Coatings by Direct Injection Into a Gas Chromatograph (D 4457-85).

Gas-Liquid Chromatography

Various terms such as gas-partition, vapor-phase-partition, gas-liquid-partition chromatography, and vapor fractometry have been used interchangeably when referring to GLC. However, the name GC, which stands for gas chromatography, is probably the most commonly used.

GLC is characterized by the presence of a stationary liquid phase, usually a nonvolatile liquid or solid that is liquid at the operating temperature, supported by the wall of a tube or by sorption to an inert porous material such as diatomaceous earth. In GLC, the components to be separated are vaporized at the entrance of a partition column and moved through the column by a continuous flow of inert gas. For the most part, the rate of migration exhibited by components is dependent upon their degree of solubility in the immobile liquid phase. Very soluble molecules are dissolved readily by the stationary phase, and their passage through the column is retarded. Compounds that have poor or moderate solubility in the liquid phase spend more time in the carrier gas and move through the column rapidly. Ideally, the multiplicity of variable conditions can be regulated so that each compound will reach the end of the column at different times where they are detected electronically as they leave the column.

The distribution of a compound between phases is referred to as its partition coefficient. Although the partition coefficient difference may be very small in a static experiment where only one equilibrium occurs, separation is possible through magnification of that difference by a continuous series of equilibria that is the normal occurrence during chromatographic separation. Since the partition coefficient is affected directly by the solubility characteristics of the liquid phase, the equilibrium for a given compound can be shifted by using stationary phases at different chemical structures. Liquid phases of varying polarity are available in great number, and it is the exploitation of their different selectivities that accounts for the tremendous flexibility and effectiveness of GLC.

Apparatus and Technique—The essential components of a gas chromatograph are shown schematically in Fig. 4. In the following discussion of equipment, it will be convenient to explain the process under its operational stages, which may be briefly summarized as follows. The flow of gas, usually from a compressed gas cylinder, is adjusted to desired levels with a series of pressure and flow regulators and split into two streams; one is allowed to flow through the reference side of a differential detector and the other is directed to the injection system, which is located immediately ahead of the column. This segment of the chromatograph, the injection port or flash vaporizer, is maintained at a temperature sufficiently high to cause instantaneous vaporization of the sample in the flowing carrier gas. Introduction of liquids and solids in solution is accomplished most often by injection through a self-sealing silicone rubber septum with a hypodermic syringe. The sample is carried immediately onto the column where the various components are separated by virtue of their different partition coefficients. As the components emerge from the partition column, they pass through a sensing device that transmits an electronic signal proportional to the concentration of the sample to a potentiometric strip recorder or an electronic integrator.

To provide maximum performance and flexibility, the injection port, column oven, and detector should all be individually thermostated. A rule of thumb is that the temperature of the injection system and detector should be at least 25°C higher than that of the column.

The choice of carrier gas is limited to a few inert gases, and this is restricted even more by the type of detector used. The most widely used carrier gases are helium, nitrogen, hydrogen, and argon.

A GC detector must be capable of sensing minute changes in the composition of the carrier gas in a reproducible and precise manner. In order to perform effectively, GC detectors must have high sensitivity, linear response, and low noise level. Secondary factors such as low cost, simplicity, and ruggedness are also desirable. The two most prominent detectors are thermal conductivity (TC) and flame ionization (FID). TC detectors, also called katharometers, consist of two filaments heated electrically and arranged in a Wheatstone bridge circuit; one filament is exposed to pure carrier gas and the other is located in the carrier gas stream emerging from the analytical column. When the carrier gas from the column

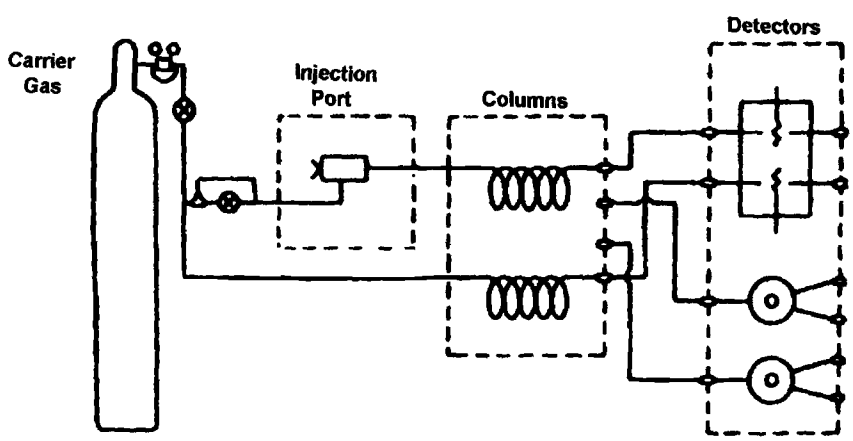

FIG. 4–Schematic diagram of a gas chromatograph.

is diluted with the sample, the temperature and resistance of the sensing filament increases, thereby causing a voltage drop across the bridge, which is shown as a peak on the chromatogram. FID detectors operate on the principle that relatively few ions are formed when hydrogen is burned in air; but when organic compounds are present, ions proportional to the carbon concentration are formed. By applying a potential across two electrodes surrounding the flame, the ion current produced from the sample molecules is fed to an electrometer amplifier, the output of which is sent to a recorder. TC and FID detectors are both durable and relatively trouble free. TC detectors will respond to virtually all compounds, whereas FID detectors are sensitive to organic compounds only. One of the principal virtues of FID detectors is its high sensitivity, about 1000 times that of thermal conductivity. Testing of thermal conductivity and flame ionization detectors used in gas chromatography are discussed in ASTM Practice for Testing Thermal Conductivity Detectors Used in Gas Chromatography (E 516-91) and ASTM Practice for Testing Flame Ionization Detectors Used in Gas Chromatography (E 594-77), respectively.

There are other high-performance detectors that are used in conjunction with GC. Beta-ray ionization detectors use a radioactive source to ionize the argon carrier effluent from the column. Metastable argon ions collide with sample molecules, inducing a current flow that is amplified and measured. Glow discharge detectors operate on the principle that the composition of the effluent can be measured in terms of voltage across a gaseous discharge. In an electron capture detector, nitrogen is passed through an ionization chamber containing tritium as the source of ionizing radiation. All ions formed by the ionizing radiation can be collected by applying a small potential across the chamber. When the effluent from a gas chromatograph contains electron-attracting compounds, a decrease in current flow proportional to the electron affinity of the compound is observed. The detector is highly selective for compounds containing halogen, conjugated carbonyl, nitriles, nitrates, and organometal compounds. The function and performance of various detectors have been discussed in detail [*53,54*]. The use of electron capture detectors in GC is covered in ASTM Practice for Use of Electron-Capture Detectors in Gas Chromatography (E 697-91). Testing of nitrogen/phosphorous thermionic detectors for use in gas chromatography is discussed in ASTM Practice for Testing Nitrogen/Phosphorus Thermionic Ionization Detectors for Use in Gas Chromatography (E 1140-86).

Most modern instruments are equipped for linear programmed temperature operation, which consists of increasing the column temperature at a uniform rate throughout an analysis. Programmed temperature gas chromatography (PTGC) is particularly useful for the examination of complex mixtures and wide-boiling-range samples, where a single analysis of high and low boiling components at constant-temperature isothermal analysis is not practical. Generally, when the range of boiling points in a mixture is 100°C or more, temperature programming is recommended. If low-temperature isothermal analysis is used, low boiling compounds will be usually separated effectively but high boiling compounds emerge as broad peaks. At high isothermal temperatures, light components emerge rapidly, causing peaks to be crowded; high boiling compounds produce favorably shaped peaks. when temperature-programmed operation is employed, a low initial temperature can be used for the separation of low boiling materials, and, by steadily increasing the column temperature, intermediate and high boiling components can be eluted in a reasonable length of time as sharp, well-defined peaks.

Although PTGC has greatly enhanced the usefulness of gas chromatography, its practice is somewhat restricted by the type of liquid phase employed. During temperature programming, a temperature is reached at which volatilization or decomposition of the liquid phase occurs, thereby causing a positive deviation of the recorder pen from the baseline. This effect is referred to as column bleeding, and in the event of severe bleeding the recorder pen may travel off-scale, obscuring any component peaks that may be present. Column bleed may be suppressed by favoring thermally stable liquid phases and through the use of short and low-loaded columns. These remedies are not always practical since a specific problem may dictate the use of conditions contrary to those described above. A more direct way to compensate for column bleed is through the use of a dual column gas chromatograph. In this type of system, a column matching the one used for analysis is mounted in the oven compartment and connected to the reference side of the detector. As the temperature is increased, a signal is generated in the reference cell equivalent to that in the sample cell, thereby cancelling out any signal due to substrate bleeding.

Columns

The successful practice of GLC depends primarily on the proper selection and preparation of a suitable column. The availability of hundreds of liquid phases and numerous solid supports in addition to parameters such as length, diameter, amount of liquid phase, and mesh size offers an almost infinite number of possibilities. Fortunately, most separations can be performed on relatively few columns involving only a few liquid phases. Columns are divided into two major classes, packed and open tubular. Packed columns consist of tubing filled with size-graded support material impregnated with a nonvolatile liquid. Generally, higher-column performance is obtained with small-column-diameter and light-stationary-phase loading. Four to ten-foot (1.22 to 3.048 m) columns of ⅛ or ¼ in. (3.175 or 6.350 mm) outside diameter containing 10 to 20% liquid phase are common.

With Golay's development of the capillary column or open tubular column [*55*], the separations possible in GLC were greatly increased. These columns are prepared by coating the inside surface of small-diameter tubing with a thin layer of nonvolatile liquid. Capillary columns are generally much more efficient than packed columns, but, owing to their low capacity, high-sensitivity detectors and special sampling techniques are necessary to accommodate the small samples used. Fortunately, the split/splitless injector ports introduced by GC manufacturers the late 1980s and early 1990s are able to handle normal-sample-size injections without much difficulty.

The readers may find the chemically cross-linked and surface-bonded stationary phases made using fused silica capillary tubing (30 m by 0.25 mm ID) quite useful to have in their gas chromatography laboratory (see Table 1).

TABLE 1—Commonly used stationary phases in the gas chromatography laboratory.

Stationary Phase Composition	Comparable to
100% dimethyl polysiloxane	DB®-1, Rtx®-1, HP®-1, OV®-1, SP-2100, 007-1
95% dimethyl-5% diphenyl polysiloxane	DB®-5, Rtx®-5, HP®-5, OV®-5, SPB-5, 007-2
80% dimethyl-20% diphenyl polysiloxane	Rtx®-20, OV®-7, SPB-20, 007-7
65% dimethyl-35% diphenyl polysiloxane	DB®-35, Rtx®-35, OV®-11, 007-11
50% dimethyl-50% diphenyl polysiloxane	DB®-17, Rtx®-50, HP-17, OV®-17, SP-2270, 007-17
50% dimethyl-50% cyanopropyl	DB®-23, SP-2330, 007-CPS-1
50% dimethyl-50% trifluoropropyl	DB®-210, SP-2410, RSL-700
50% dimethyl-50% cyanopropyl phenyl polysiloxane	DB®-225, Rtx®-225, HP-225, OV®-225, 007-225
cyanopropyl-phenyl-dimethyl polysiloxane	DB®-624, 007-624, AT-624, OV®-624, Rtx®-volatiles
86%-dimethyl-14% cyanopropyl phenyl polysiloxane	DB®-1701, Rtx®-1701, OV®-1701, 007-1701
100% biscyanopropyl polysiloxane	Rtx®-2340, SP-2340, OV®-225
acidified polyethylene glycol	DB®-FFAP, HP-FFAP, 007-FFAP, SUPEROX®-FA, OV®-351, STABILWAX®-DA
polyethylene glycol	DB®-WAX, STABILWAX®, HP-20M, 007-CW, SUPEROX® II, SUPELCOWAX®

NOTE:

Trademark	*Company*
DB®	J&W Scientific
OV®	Ohio Valley Specialty Chemical
Rtx®	Restek Corporation
STABILWAX®	Restek Corporation
SUPEROX®	Alltech Associates
SUPELCOWAX®	Supelco, Inc.
Teflon®	E. I. du Pont de Nemours & Co., Inc.

Tubing

Tubing materials should be stable with respect to the sample, packing, and carrier gas, and be of uniform diameter. Tubing made of copper, stainless steel, monel, glass, and plastic have all been used for the construction of packed columns. The two most widely used materials are stainless steel and copper—stainless steel for its inertness and copper for its low cost. The most common tubing material used in capillary column gas chromatography is fused silica, primarily due to its flexibility and inertness. Special attention was given to the wide-bore, 0.53-mm inside-diameter columns because they have been reported [*47*] as a packed column alternative. Readers are also referred to a 1990 review covering the fundamentals, characteristics, and selection of open tubular columns in gas chromatography [*48*].

Solid Support

The function of the support material is to provide a large surface area for holding the liquid phase; it should be chemically inert to the sample and partition liquid and have good handling characteristics. The principal support materials are those derived from diatomaceous earth (Table 2). They are relatively inert, have adequate mechanical strength, and will adsorb up to 40% of the liquid phase without losing their free-flowing character. Diatomaceous earth supports can be broadly classified as to color: white or pink. White supports contain fewer active sites and therefore are considered superior for the analysis of polar compounds. Pink supports, on the other hand, are less fragile and have a greater capacity for holding the liquid phase. Schuppe and Lewis [*49*] group the

TABLE 2—Commercial diatomaceous solid support materials [*44*].

Solid Support			
White			Pink
ASTM Code 50	ASTM Code 60	ASTM Code 70	ASTM Code 80
Anakrom U	Chromosorb G	Celatrom	Anakrom P
Celite 545		Gas Chrom S	Chrompak P, Regular
Chrompak W, Regular			Chromosorb P
Chromosorb W			Columpak
Chromaport			Firebrick, C-22
Diatoport W			Gas Chrom R
Embacel			GC Super Support
Gas Chrom Cl			Sterchamol
			Ultraport

various commercial diatomaceous earth supports according to color and ASTM code.

Ideally, a support should be completely inert, but unfortunately diatomites exhibit a certain amount of surface activity. The interaction with polar compounds, usually hydrogen bonding, is attributed mainly to the presence of silanol (—Si—OH) groups located at the surface of the support. Attempts to deactivate supports have been practiced in several ways: washing with acid and alkali, saturating with polar liquids, and reacting silanol groups with reagents. Although acid and base washing have been widely practiced, both techniques are of questionable value. In fact, acid treatment has sometimes proved deleterious by promoting isomerization of certain compounds and the decomposition of the liquid phase. By far the most effective way to reduce support reactivity is by reacting the silanol groups with a silylating reagent. This treatment is more effective with white supports; the degree of deactivation varies with the type of reagent and the technique employed.

Other support materials of notable importance are glass beads, Teflon®, and porous polymers. Since porous polymers are used generally without a liquid phase, they will be discussed in detail under gas solid chromatography. Teflon® has found its greatest use in the separation of very polar compounds such as water, acids, alcohols, and amines, but Teflon® has poor handling properties and produces columns that are much less efficient as compared to columns from diatomaceous earth. Because of their low surface area, glass beads can not hold much liquid phase, less than 0.5%; it is this low volume of liquid phase that is responsible for some of its advantages, namely, speed of analysis and low operating temperatures. They are, on the other hand, substantially less efficient than diatomite columns. For information concerning support technology, such as types, physical properties, chemical structure, pore structure, treatment, etc., the reader is referred to detailed articles [*56–58*] on the subject.

Stationary Liquid Phase

The selection of liquid phase is one of the most vital judgments made in selecting a chromatographic system, for it is the degree of selectivity of the partitioning liquid that most strongly influences the separating capability of a GLC column. Theoretically, any liquid can be used as a liquid phase, but there are some limiting factors. A liquid phase must be nonreactive to the system and sample, have reasonable thermal stability, and be liquid at the operating temperature. Although materials of low vapor pressure are favored, the main criterion regarding volatility is that the liquid phase be relatively nonvolatile (vapor pressures 0.01 to 0.10 mm) at operating temperature. Finally, a liquid phase must be soluble in some volatile solvent to allow coating of the support. Terms such as substrate, partition liquid, stationary phase, and solvent are synonymous with liquid phase.

Considerable effort has been expended in an attempt to permit advance prediction of the most suitable liquid phase for a given problem, but most often the analyst must rely on experience, published procedures, and certain generalizations. Although solute-liquid phase activity such as chemical interaction, hydrogen bonding, and other cohesion forces all affect the selectivity of the liquid phase, in practice the most distinguishing characteristic is polarity. The polarity of the liquid phase is determined by the ratio of polar or polarizable groups to nonpolar groups, with the retention of solutes depending on the relative polarities of solutes and liquid phase. The greater the polarity of the stationary phase, the greater is the solubility (retention) of polar solutes relative to nonpolar solutes. The solubility or lack of solubility of sample components in the liquid phase can be used to make group separations or to accelerate or retard components with respect to others in the sample. In general, nonpolar liquid phases separate nonpolar solutes by order of volatility and polar solutes by structural type; whereas, polar phases separate polar solutes by order of relative volatility and polarity and nonpolar solutes by structural type.

An enormous number of liquids, semisolids, and solids have been recommended for use as liquid phases. Schupp [*54*] listed over 300 materials along with their maximum temperatures, chemical names, and trade names. The seventh edition of *Guide to Stationary Phases for Gas Chromatography* [*59*] contains over 700 literature references to liquid phase use in order of application to different classes of compounds. Lists of liquid phases, arranged alphabetically in chemical classes, are available from suppliers of chromatographic equipment, and they usually include maximum temperatures and solvency. Although there are a vast number of liquid phases available, the majority of problems encountered in most laboratories can be resolved with five or six stationary liquid phases provided they represent a wide range of polarities. The following list, arranged in order of descending polarity, is representative of such a group: N,N bis(2-cyanoethyl)formamide; diethylene glycol succinate; dodecyl phthalate; polyethylene glycol (molecular weight 20 000); and apiezon grease. Books on GLC generally contain chapters devoted specifically to the discussion of partition liquids, and it is recommended that the reader consult the previously mentioned books [*54,65*] for a more complete study of liquid phase technology.

Column Efficiency

Column efficiency may be defined by considering the narrowness of a peak relative to time spent in the column. Provided there are no instrumental deficiencies, column efficiency is a function of packing type, packing technique, and operating conditions and is usually expressed in terms of the number of theoretical plates. The plate concept, a carryover from countercurrent extractions, implies a series of complete equilibria or "theoretical plates." The better the performance of a column, the higher is its number of theoretical plates. Inasmuch as distinct stages are not observed in chromatographic separations, the number of theoretical plates for a column is calculated from the relative peak sharpness shown on the chromatogram. A good packed column should have an efficiency of at least 400 plates, and it is not uncommon for a well-prepared column to have over 1000 plates. The number of theoretical plates, N, equals $16(x/y)^2$, where x is the distance in millimeters from injection to peak maximum, and y is the baseline in millimeters cut by the two tangents as shown in Fig. 5.

Column efficiency can be expressed per unit of column length. The height equivalent to a theoretical plate (HETP) is calculated by dividing L, the length of the column in centimeters, by N; thus, HETP = L/N. High HETP indicates that the

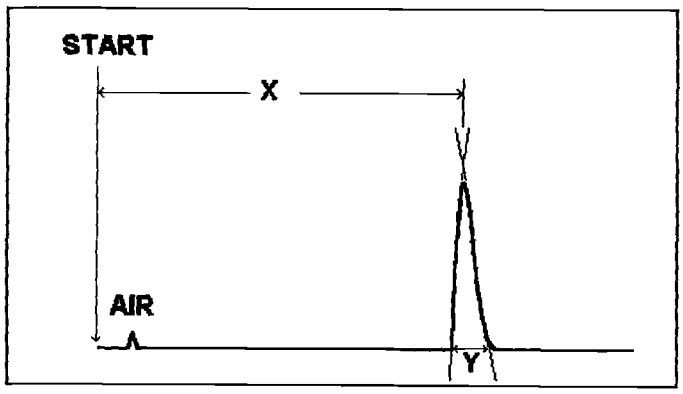

FIG. 5–Graphic calculation of column efficiency.

column has been poorly prepared or is not being operated under ideal conditions.

Theories [*60–62*] have been developed to elucidate mechanisms that cause spreading of the component molecules as they pass through the column, and an understanding of such processes is important to efficient operation of a chromatograph. Such theories take into account the interrelated multiple effects of parameters such as column diameter, column length, carrier gas, temperature, gas velocity, support size and shape, and sample size, and their ultimate effect on N. A summary and comparison of these theories have been presented [*63*]. A brief discussion to shorten analysis time while maintaining or improving resolution was published in 1993 [*64*].

Interpretation of Chromatograms

Fundamentally, the object of a chromatographic analysis is the resolution of sample components for identification and quantitative measurement. Fortunately, GC has tremendous capacity for resolving mixtures, but, unlike many other instrumental techniques, the record of an analytical run tells very little about the chemical nature of separated compounds. In addition, components in a sample mixture may not completely separate on a given column; consequently, the number of peaks on a chromatogram is not always an indication of the number of compounds in a sample.

When background information concerning the sample is available and when sample components are few, the interpretation of GC data is fairly simple. However, the interpretation of a chromatogram from a multicomponent sample, where background information is limited, is a formidable task. In this section, qualitative and quantitative analysis will be briefly discussed; for a more complete treatment of the subject, the reader is referred to the work of others [*65,66*].

Qualitative Analysis

For a given set of operating conditions, the amount of carrier gas required to elute a compound from a column is characteristic for that compound and is not influenced by the presence of other compounds. Accordingly, the time from injection to peak maximum is a property peculiar to a compound. This type of information, represented as retention volume (V_R) and retention time (t_R), has been the basis for most schemes of qualitative analysis. The use of such information may be greatly assisted by the considerable amount of published retention data such as ASTM compilations [*49,50*].

One of the weaknesses of gas chromatography is in the identification of unknown compounds. J. C. Dutoit [*51*] examined the retention indices of 135 solutes representing most chemical families on pure polar phase and pure nonpolar phase. This 1991 publication should aid the readers in the qualitative identification of GLC peaks. Another recent study regarding qualitative analysis by GLC using retention indexing was completed by Y. Sun et al. [*52*]. The programmed temperature retention value databases compiled in various laboratories are listed along with reproducibility data under different chromatographic conditions.

For the purpose of illustration, the description of retention parameters will be confined to retention times; this does not, however, imply the use of retention volume to be inferior. Retention time measurements are shown on the chromatogram presented in Fig. 6. The adjusted retention time (t'_R), time measured from air peak to peak maximum, corrects for instrument dead volume.

The first impulse would be to conclude that absolute retention times are adequate for identification purposes, but absolute retentions are comparable only when obtained on the same column using identical operating conditions. Instead, most retention times are calculated relative to some other compound that is used for reference. Relative retention time (r) is obtained as follows:

$$r_{c,s} = t'_{R,c}/t'_{R,s}$$

where c refers to component in the sample, and s indicates the reference standard. Relative retention times are independent of column length, liquid loading, and flow rate, but they are dependent on the type of liquid phase. The reference material may be one that is known to be in the original sample, or it can be mixed prior to the chromatographic analysis. In practice, relative retentions are obtained usually by computing the ratio of the distance from air peak to standard and air peak to component.

Once a peak has been tentatively identified from its retention time, the sample may be "spiked" with the suspected compound to see if it superimposes and shows up as one peak. If the two materials emerge together, this is good evidence of its presence in the original sample, but this does not constitute positive identification since more than one com-

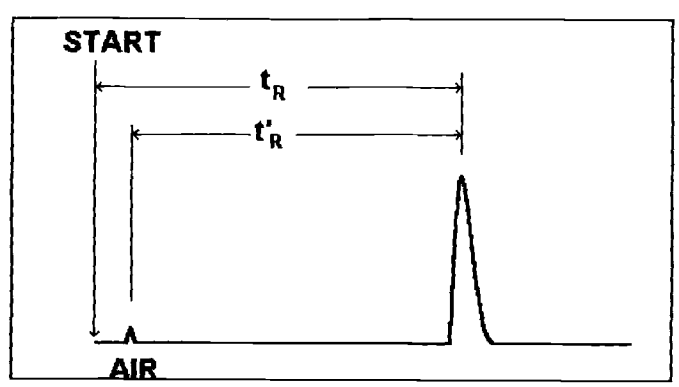

FIG. 6–Retention time (t_R) and adjusted retention time (t'_R).

pound may have the same retention time for a given column. The next step is to go through the same procedure using a different column having a packing of completely different polarity. It is not likely that two materials will have the same retention time on widely different columns, but, if doubt still persists, the compounds can be trapped at the exit of the GC unit, and the isolated materials can be subjected to instrumental or chemical analysis. Walsh and Merritt [*67*] trapped eluted materials in a neutral solvent and applied a battery of chemical tests to determine chemical functionality. Methods have been described for direct trapping of fractions on a disk of potassium bromide and fraction trapping with subsequent transfer to a microcell; the isolated components were then subjected to infrared (IR) analysis. Although somewhat limited in versatility and flexibility, table top GC-mass-spectroscopic and GC-FTIR units do an outstanding job of routine identification and for quality control purposes. Prices of these integrated instruments vary from 60,000 to approximately $100,000.

Success in any research laboratory is highly dependent on the timing upon which unknown chromatographic peaks are identified. While infrared (IR) and mass spectroscopy (MS) have been proven to be important qualitative tools, each has its inherent weaknesses. When used together, these techniques reinforce each other, producing a richer body of useful information than either technique used alone [*68*]. The use of mass spectrometers as detectors for capillary column gas chromatography has also been discussed by Clement [*69*] in his 1992 publication. Another 1992 review [*70*] with several references is given on gas chromatography, including column types, injection methods, detection means, data systems, supplementary apparatus, and future prospects.

Quantitative Analysis

The analog signal generated by the presence of a compound in the carrier gas is proportional to its concentration, and quantitative analysis is obtained by conversion of this signal to some form of digital data. For the most part, quantitative data are obtained from peak area measurements, but significant use has been made of peak heights.

Peak areas can be measured by: (1) use of a planimeter, (2) cutting and weighing chart paper, (3) triangulation ($A = WH/2$), (4) height times width at half height ($H \times W$ at $H/2$), (5) ball-and-disk type of integrator, and (6) electronic digital integrator. The planimeter yields good results, but its use is tedious, and accuracy is dependent on the shape of the peak and the skill of the operator. Cutting and weighing peaks from chart paper is time consuming, and it is practically impossible to accurately cut and weigh cutouts of narrow peaks. Triangulation and height times width at half height are both relatively simple methods, and each will yield satisfactory results with symmetrical peaks, but the methods are unsuitable with asymmetric or very narrow peaks. The ball-and-disk type of integrator, which is attached to the drive mechanism of the recorder pen, has found widespread application. Since peak areas are integrated as they are recorded, the operator need only count the integrator units under the appropriate peak. With an electronic integrator, the output from a gas chromatograph is fed to the measuring unit that converts the analog signal to digital, which is eventually converted to peak areas using appropriate algorithm. The integrated peak areas are read directly from the printer/plotters of most electronic integrators. Of the various methods for integrating peak areas, ball-and-disk and electronic integration provide the best results for applications requiring reasonable speed and precision of quantitative data. However, ball-and-disk integrators are extremely difficult to find because of the popularity of electronic digital integrators. Where cost permits, particularly in the case of routine analyses, the electronic digital integrator is preferred. Most electronic integrators made in the late 1980s and early 1990s have the capability of plotting the chromatograms in real time. Thus, a separate strip chart is no longer necessary to monitor the progress of the analysis.

Area normalization and internal standardization are methods used for converting digital data to percent composition. In the normalization procedure, the area of the component being measured is divided by the total area of all other peaks. This method assumes that all of the sample is eluted from the column.

$$\text{percent component } C = \frac{\text{area of } C}{\text{total of peak areas}} \cdot 100$$

If a portion of the sample remains on the column, error proportional to the amount of material remaining on the column will be conferred on all the compounds measured.

The internal standard method is used more widely for the quantitative interpretation of a chromatogram. In this method, peaks of interest are calculated relative to a known amount of internal standard that has been added prior to chromatography. It is not necessary to determine all peaks as in the normalization method, and this can be advantageous particularly when one compound is to be determined in a complex mixture. The following calculation is used with internal standardization determinations:

$$\text{percent component } C = \frac{C \cdot W}{B \cdot S} \cdot 100$$

where

C = peak area of component,
B = peak area of internal standard,
W = weight of internal standard, and
S = weight of sample.

If the determination is to be calculated on a volume basis, simply substitute volume for weight in W and S. Complete elution of all components is not necessary; in fact, the percent of sample hangup can be determined by calculating the total percent represented by all the peaks eluted and subtracting the total from 100.

A direct weight-to-area relationship does not exist for all compounds. Detector response is a function of structure and molecular weight; the detector response for a given compound is not the same with all detectors since various detector types operate on different principles. Once determined, however, response factors are generally interchangeable between instruments having the same type of detector. Messner et al. [*71*] published thermal conductivity factors for a large variety of compounds and also provided a formula for calculating factors. Deitz [*72*] tabulated a lengthy list of TC and FID detector response factors for various classes of compounds. For certain applications, peak height measurements

are more convenient and reliable than peak area. Such is the case when peaks are tall and narrow and where errors in area measurements are likely to be maximized. Peak height determinations are affected to a greater extent by variations of operating conditions than are peak area determinations. This effect is greatly diminished through the use of an internal standard.

To increase accuracy and precision of peak area measurements, the use of electronic integrators is highly recommended. The initial cost for such an investment can easily be recovered within a short period of time primarily through labor cost savings. Current integrators are so versatile that they can perform difficult peak integration that normally would take a less experienced analyst a lot of time to perform. Some can perform reintegration and recalculation using a variety of methods. In the 1990s, most integrators are capable of being interfaced to a personal computer to enhance data crunching and for information storage and retrieval purposes. This is especially useful where data documentation is critical.

Applications—Applications for GLC in the paint industry exist at almost every level of manufacture and product development. Its rapid acceptance by the industry is due to several inherent features, principally, versatility and speed. Initially, analyses were solvent oriented, but applications to virtually every class of material used in surface coatings have been reported in the literature. At present, GLC is used for a variety of analytical operations including both routine and research functions. It is unexcelled as a routine quality control tool for defining raw materials to be used for the manufacture of paint products. Batches of solvent, plasticizers, polyols, fatty acids, and other materials can be examined simply and rapidly to determine conformance to acceptable standards. Information regarding vehicle composition of a whole paint can be obtained in great detail and with reasonable accuracy. Moreover, GLC can be used to monitor drying processes, solvent release from films, and the chemical curing of polymeric materials. In a 1991 publication, K. Takahashi [*42*] described a simple and sensitive method for the measurement of the leaching rate of tributyltin and triphenyltin compounds from antifouling paint by gas chromatography using flame photometric detection. Static headspace analysis by combined gas chromatography–mass spectrometry for the analysis of organic solvents in printing inks was recently studied [*43*].

Because of the multiplicity of published papers relevant to GC coatings analysis (well over 1000), complete coverage of all applications is beyond the scope of this chapter. A review [*46*] describing basic GC processes and applications includes approximately 150 references to coatings analysis. In his monograph on GC application to polymer analysis, Stevens [*44*] refers to several hundred analytical procedures and, in many cases, presents operating conditions, tables of retention times, and chromatograms. Readers are directed to the second part of a 1992 article by Ettre [*45*] on the evolution of chromatography since the development of GLC by Martin and James 40 years ago and HPLC by Moore and Horvath 25 years ago.

A partial list of references is shown in Table 3; examples were selected to illustrate the variety of coating problems amenable to GLC analysis. Methods directed to the analysis of oils and fats are listed separately, but most are also applicable to fatty acids isolated from alkyd resins. A compilation of ASTM methods that have been evaluated and accepted as standard or tentative procedures is presented in Table 4. Other GLC procedures are currently being evaluated for ASTM acceptability.

One facet of GLC that often goes unrecognized is the pretreatment of substances to alter their structure, thereby permitting the examination of materials that would not respond normally to GLC analysis. Such is the case with the analysis of paint binders and very polar materials such as polyols and dicarboxylic acids. Many of the methods of sampling and techniques for preparing derivatives described by Cavagnol and Betker [*73*] and Schupp [*74*] have application to the analysis of surface coatings. Beroza and Coad [*75*] attack the same general problem but in a different way; for the most part, samples are altered within the instrument and not externally.

In the following discussion of analytical methods, special emphasis will be directed to the broad range of usefulness within the paint field, and, wherever possible, basic principles and equipment will be stressed.

Solvents

A major consideration in GLC is sample volatility. Materials to be analyzed must possess sufficient vapor pressure to permit vaporization at the point of sample introduction. Since enamel and lacquer solvents fulfill this requirement, it is only natural that GLC would be rapidly utilized in this area. Solvents may be encountered in two forms: as raw material to be formulated into a surface coating or as an ingredient of a coating. In the latter event, the analysis is complicated by the presence of pigment and binder, which usually necessitates the isolation of solvent through distillation. To alleviate problems associated with solids or nonvolatile components of the paint or coating, a removable glass liner or glass insert can be installed in the injection port of the gas chromatograph. Such glass liners can be occasionally solvent-cleaned or oven-cleaned overnight at 400°C. Another, but less desirable alternative, is through the use of a precolumn. The precolumn should be made from the same stationary phase as the analytical column.

An important aspect of production control is the analysis of individual solvents for impurities. Relatively small amounts of impurity may seriously affect the performance characteristics of a paint, and such impurities can be easily detected and determined using GLC. Batches of solvent can be rapidly screened by subjecting them to GLC analyses and comparing the resulting chromatograms to those obtained from reference materials of acceptable quality. Relative amounts of each solvent can be quickly ascertained from ratios of peak heights or peak areas. If significant deviation from the reference material is observed, a more thorough and precise GLC analysis can be then conducted. In 1993, Vonk [*78*] described the use of wide-bore fused silica columns for the analysis of solvents.

Petroleum fractions, such as mineral spirits and VM&P naphtha, are extremely complex mixtures of hydrocarbons, and it is virtually impossible to completely separate all the components. Nevertheless, valuable information regarding

TABLE 3—Gas chromatographic methods relevant to organic coatings analysis.

Subject	References
Reviews	*37, 38, 39, 40, 41, 44, 45, 46, 47, 48, 68, 70, 138*
Solvents	*76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 137*
Oil and fatty acids	*91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101*
Resin acids	*102, 103, 104*
Alkyd and polyester resins	
Fatty acids	*105, 106, 107*
Dicarboxylic acids	*108, 111, 112, 113, 114*
Polyols	*108, 112, 113, 115, 116, 117*
Pyrolysis	*109, 110, 118, 119, 120, 121, 122, 123, 124, 125, 126*
Plasticizers	*127, 128, 129, 130*
Residual reactants	*131, 132, 133, 134, 142*
Volatile organic compounds (VOC)	ASTM D 3792, ASTM D 3960, ASTM D 4457
Miscellaneous	*43, 135, 136, 137, 139, 140, 141, 142, 143, 144, 145*

TABLE 4—Summary of ASTM test methods for paints, related coatings, and aromatics using gas chromatography.[a]

D 1983	Test Method for Fatty Acid Composition by Gas-Liquid Chromatography of Methyl Esters
D 2245	Method for Identification of Oils and Oil Acids in Solvent-Reducible Paints
D 2306	Methods for C_8 Aromatic Hydrocarbon Analysis by Gas Chromatography
D 2360	Test Method for Trace Impurities in Monocyclic Aromatic Hydrocarbons by Gas Chromatography
D 2455	Test Method for Identification of Carboxylic Acids in Alkyd Resins
D 2456	Test Method for Identification of Polyhydric Alcohols in Alkyd Resins
D 2743	Practices for Uniformity of Traffic Paint Vehicle Solids by Spectroscopy and Gas Chromatography
D 2800	Test Method for Preparation of Methyl Esters from Oils for Determination of Fatty Acid Composition by Gas Chromatography
D 2804	Test Method for Purity of Methyl Ethyl Ketone by Gas Chromatography
D 3008	Test Method for Resin Acids in Rosin by Gas Chromatography
D 3009	Test Method for Composition of Turpentine by Gas Chromatography
D 3054	Test Method for Purity and Benzene Content of Cyclohexane by Gas Chromatography
D 3257	Test Methods for Aromatics in Mineral Spirits by Gas Chromatography
D 3271	Methods for Direct Injection of Solvent-Reducible Paints into a Gas Chromatograph for Solvent Analysis
D 3329	Test Method for Purity of Methyl Isobutyl Ketone by Gas Chromatography
D 3362	Test Method for Purity of Acrylate Esters by Gas Chromatography
D 3432	Test Method for Unreacted Toluene Diisocyanates in Urethane Prepolymers and Coating Solutions by Gas Chromatography
D 3457	Test Method for Preparation of Methyl Esters from Fatty Acids for Determination of Fatty Acid Composition by Gas-Liquid Chromatography
D 3545	Test Method for Alcohol Content and Purity of Acetate Esters by Gas Chromatography
D 3626	Test Method for Tar Acid Composition by Gas-Liquid Chromatography
D 3760	Test Method for Analysis of Isopropyl Benzene (Cumene) by Gas Chromatography
D 3792	Test Method for Water Content of Waterborne Paints by Direct Injection Into a Gas Chromatograph
D 3797	Test Method for Analysis of *o*-Xylene by Gas Chromatography
D 3798	Test Method for Analysis of *p*-Xylene by Gas Chromatography
D 3893	Test Method for Purity of Methyl Amyl Ketone and Methyl Isoamyl Ketone by Gas Chromatography
D 3960	Practice for Determining Volatile Organic Content (VOC) of Paints and Related Coatings
D 4367	Test Method for Benzene in Hydrocarbon Solvents by Gas Chromatography
D 4457	Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection Into a Gas Chromatograph
D 4492	Test Method for Analysis of Benzene by Gas Chromatography
D 4534	Test Method for Benzene Content of Cyclic Products by Gas Chromatography
D 4735	Test Method for Determination of Trace Thiopene in Refined Benzene by Gas Chromatography
D 5135	Test Methods for Analysis of Styrene by Capillary Gas Chromatography

[a]*Annual Book of ASTM Standards,* Volume 06.01.

the nature and identity of such solvent systems may be obtained by comparison with reference chromatograms obtained using identical operating conditions. No attempt is made to identify the individual peaks; instead, observations are made to determine if the unknown and control have similar distillation ranges and if peaks are proportional. Chromatograms of this type are referred to as "fingerprints" and will often suffice for quality control purposes.

The percentage of aromatic species in mineral spirits may be determined by using columns prepared from highly selective liquid phases such as N,N-bis(2-cyanoethyl) formamide (CEF) and 1,2,3-tris(2-cyanoethoxy) propane. These very polar liquid phases are capable of eluting high boiling aliphatic solvents well in advance of low boiling aromatics, thereby providing the means for aliphatic-aromatic group separation. Such columns provide the basis for the analysis of aromatics in enamel thinners and solvents [*79,80*] yielding information that relates to the photochemical reactivity of hydrocarbon solvents, a factor of importance in air pollution studies.

The problem of determining solvents in whole paints and lacquers by GLC is compounded by the presence of nonvolatiles, and special provisions must be made for sampling. No universal method for isolating solvent from paint and lacquer is available. Vacuum distillation and collection in a cold trap [*86*] works well in many cases, but this scheme is time-consuming and difficulties arise when very light or very heavy solvents are present. Introduction of a coating from a syringe onto an adsorbent pad [*36*] in the injection port has been used, but viscous samples require dilution, and thermally unstable resins are decomposed in the injection port, resulting in the appearance of extraneous peaks on the chromatogram. To avoid or significantly minimize thermal degradation of certain resins, it is advisable to decrease the injection port temperature below its decomposition temperature. A good injection port temperature for most solvent analysis is 200°C. As previously indicated, use of a removable glass liner or insert is a must if direct injection of the whole paint is to be performed. Again, the glass insert can be occasionally cleaned using an appropriate solvent or by overnight oven cleaning at 400°C. Precipitation of lacquer resins with pentane and subsequent analysis of the supernatant liquid by GLC works well with most automotive lacquers [*77*], but the nonuniform occlusion of certain solvents has been reported. For the most part, the means of sample handling will be determined by the type of material encountered and the extent of analytical information desired.

Several comprehensive schemes have been proposed that are particularly useful for the analysis of unknown samples. Haken and McKay [*87*] used GLC in conjunction with solubility tests in various media along with functional group analysis for the characterization of solvent systems. The New York Society for Paint Technology published a paper [*81*] on the subject of solvent analysis that included a comprehensive tabulation of retention data for a broad spectrum of solvents. A procedure for the identification of plastic and lacquer solvents was described by Haslam et al. [*86*]. The solvents were isolated by vacuum distillation in a sealed "H-tube" and subsequently separated on tritolyl phosphate and paraffin wax columns. Chromatographic data were supplemented by infrared spectroscopy where necessary.

Since no single column will separate all solvents, separation on one liquid phase can be very misleading. When examining an unknown solvent mixture, it is best to conduct the analysis on at least two liquid phases of different polarity, and in some cases supplementary chemical or instrumental testing will be also necessary.

GLC has been also used to study the retention of solvents in paint films during drying processes [*88,89*]. It has been demonstrated that solvent retention is related to the chemical structure of the film and solvent, as well as the boiling point of solvents. Perrone [*90*] also described a GC method for the determination of residual solvents in pressure sensitive tapes as a quality control step in the manufacturing process.

Oils

The drying and nondrying oils used in the production of paints and varnishes can be identified through the application of GLC. The GLC analysis is preceded by the saponification of sample and isolation of the fatty acids. Free fatty acids may be examined directly [*100*], but they are generally analyzed as their methyl esters, which are more volatile, less polar, and less susceptible to isomerization. Any of several acid-catalyzed esterification techniques, for example, hydrochloric acid (HCL), sulfuric acid (H_2SO_4), or boron trifluoride (BF_3) in methanol, will provide adequate conversion to the ester; the BF_3-methanol reagent, however, offers the advantages of a high yield combined with rapid ester conversion. The difficulty in handling BF_3 gas can be circumvented by using boron trifluoride etherate in methanol. The reagent is easy to prepare, stable, and will convert fatty acids to their corresponding methyl esters within a few minutes.

Many of the fatty acids found in oils are of the same carbon chain length, differing only in position and number of double bonds. Most polyester liquid phases will differentiate between C_{18} fatty acids, but polyesters having the highest oxygen-to-carbon ratio provide the best separations. Of the polyester liquid phases, diethylene glycol succinate has received the most attention. Six-to-eight-foot (1.83 to 2.44 m) columns containing 10 to 20% polyester on white diatomaceous earth supports are most common.

Zielinski et al. [*105*] considered the analysis of reacted and unreacted oils and made provisions for their complete analysis. Fatty acids were identified from the relative retention time ratio (RTR) values. RTR values were defined as the numerical ratio of the corrected retention time of a given methyl ester peak to that of the methyl palmitate peak. With the exception of licanic and eleostearic acids, all the fatty acids can be readily separated and identified.

Linseed, soybean, tall, safflower, and cottonseed oils can be identified from their characteristic fatty acids distributions. With other oils, identification may be achieved from an inspection of only one or two acids. For example, marine oils contain respectable amounts of palmitoleic and myristic acids, castor oil consists mostly of ricinoleic acid, coconut oil is rich in lauric acids, and oiticica and tung oils contain appreciable amounts of licanic and eleostearic acids, respectively.

Complete details for the identification of oils in organic coatings by GLC may be found in ASTM Test Method for Fatty Acid Content of Alkyd Resins and Resin Solutions

(D 1398), ASTM Test Method for Fatty Acid Composition by Gas-Liquid Chromatography of Methyl Esters (D 1983), and ASTM Test Method for Identification of Oils and Oil Acids in Solvent-Reducible Paints (D 2245). The first provides a means of isolating fatty acids from an alkyd resin, and the other two give details for preparing methyl esters, chromatographic analysis, and interpretation of data.

A further extension of GLC to fatty acid analysis is demonstrated in a method for dimer acids [*107*]. Dimer acids are relatively nonvolatile, but their elution as methyl esters is made possible by using a short column composed of a thermally stable liquid phase, silicone grease, on silanized Chromosorb W. Monomeric fatty acids are eluted as one peak, while dimer acids emerge further along the column as a well-defined gaussian peak.

Resins

The GLC analysis of resins constitutes a special problem inasmuch as the analyst must rely on some means of forming volatile products, either by derivative formation or through thermal decomposition. Thermal decomposition techniques will be discussed in greater detail in the following section; this section will be concerned with methods for converting nonvolatile resinous materials to volatile derivatives.

Alkyd and polyester resins account for a large portion of polymeric material used in organic coatings. The identification of the oil component in alkyd resins by GLC has been already described. The remaining classes of material, dicarboxylic acids and polyols, can be analyzed by chemically degrading the resin so as to regenerate the acids and alcohols, which are then derivatized and subsequently analyzed by GLC. If butylamine is used to degrade the resin, polyols may be analyzed qualitatively [*115*] as their acetates or qualitatively and quantitatively as trimethylsilyl ethers [*117*]. The latter method involves a minimum of sample manipulation, and it is applicable to all of the polyols normally found in alkyd resin. Both procedures are relatively uninvolved and capable of analyzing more than one polyol simultaneously.

When alkyd or polyester resins are subjected to a catalyzed equilibrium reaction in a large excess or methanol, methyl esters of mono- and dicarboxylic acids are formed in good yield.

$$\text{MeOH (large excess)} + \text{alkyd or polyester} \longrightarrow \text{methyl ester} + \text{glycol}$$

A method [*111*] has been developed for the identification of mono- and dicarboxylic acids in alkyd and polyester resins where lithium methoxide was employed as the transesterification catalyst. Two columns, one polar and the other nonpolar, were used to obtain retention data. Identification was made possible by comparing the relative retention times of peaks from a sample to those obtained from pure compounds. Percival [*108*] reported a similar method using sodium methoxide as the catalyst; semiquantitative results for polyols and dicarboxylic acids were presented.

Pyrolysis

Thermal degradation, when used in conjunction with GLC, can be applied to the analysis of a wide range of polymeric materials. This technique, commonly referred to as pyrolysis, has been the subject of numerous papers. One of the most recent reviews regarding pyrolysis gas chromatography, their advantages and problems in polymer characterization, was published in 1992 by Ahmadi et al. [*109*]. Pyrolytic GLC is a most convenient way of analyzing small quantities of high-molecular-weight material without the necessity of resorting to chemical pretreatment. Under proper conditions the products of thermal degradation are unique for the material being analyzed, and if conditions are controlled carefully, highly reproducible results are obtained. Data, however, are sometimes difficult to interpret, and reproducibility between laboratories is not always good.

Early pyrolysis work was conducted in a system external to the gas chromatograph, with the pyrolyzate being collected in a cold trap. Pyrolysis products were introduced into a gas chromatograph and chromatographed by conventional means. Ever since its inception, pyrolytic GLC has undergone a series of refinements with the ultimate development of integrated pyrolytic-GLC systems. Curie point pyrolysis coupled with gas chromatography–mass spectrometry (GC-MS), headspace GC-MS, and preparative HPLC were used to determine the compounds of an uncured polyester resin containing a cross-linking accelerator, an acrylate copolymer, surfactants, additives, and marble powder [*110*]. Of the many techniques described in the literature, two are most prominent.

In one method, a filament of high-resistance wire is coated with the sample resin, and the sample is pyrolyzed by energizing the filament with a predetermined amount of current. In a modification of the "filament technique," a quartz or ceramic sample holder is placed inside the heating coil to prevent catalysis, which may occur at the surface of the wire. In both variations, pyrolysis products are carried onto the column as they are formed, thus preventing the occurrence of secondary reactions between highly reactive chemical species. Pyrolysis temperature can be controlled by calibrating various settings of a variable voltage source with a thermocouple.

The second type of pyrolysis [*119*] employs a microoven to decompose the sample. In this technique the oven is preheated to the desired reaction temperature and the sample is then introduced by means of a moveable boat or cup. The unit can be designed so that several samples can be readied for analysis and introduced one at a time by external sample manipulation. Generally, the carrier gas is not allowed to flow over the sample until pyrolysis is complete, at which time valves are positioned so as to direct the carrier gas flow over the boats, thereby carrying the pyrolysis products onto the column.

As compared to the filament technique, the microoven offers better reaction temperature control and a means of weighing the sample and residue, but it is more susceptible to secondary reaction of pyrolysis products.

Since polymer composition may vary over a wide range, it is difficult to choose column and chromatography conditions to cover all substances. Some polymers yield highly polar species (for example, acetic acid from polyvinyl acetate or amines from nitrogenous resins) that may be lost by adsorption on the column. Columns that perform well with polar substances are not always suitable for the separation of less

polar materials. Therefore, optimum conditions should be determined for different classes of polymers. When samples are completely unknown, best use is made of pyrolysis when the general type of resin is determined by prior chemical or instrumental testing. Kim [*120*] reviewed the fundamentals of gas chromatography and pyrolysis and their applications in the analysis of fibers and polymers. Generally, the fragmentation of polymers will proceed by three basic pyrolytic reactions. Cross-linked polymers tend to carbonize, and as a result they produce pyrograms that are very difficult to relate back to the starting material. Such is the condition with alkyd resins. Secondly, some linear polymers will rupture between the side chain and the polymer backbone. This type of pyrolysis can be useful if the decomposition products are characteristic of the side chain. Pyrolysis of polyvinyl acetate typifies this type of bond schism; acetic acid is the principal decomposition product. The final and most useful type of pyrolysis occurs when the polymer backbone ruptures, producing monomers of the polymer. This type of decomposition is favored by quaternary-substituted carbons on the polymer backbone. For instance, good yields of methacrylate monomer are formed from the pyrolysis of polymethacrylate polymers, whereas polyacrylate polymers give low yields of acrylate monomer.

If experimental conditions are controlled carefully, the reproducibility of pyrolysis patterns is good. Thus, if sufficient reference chromatograms are developed, an unknown resin can be identified by matching the sample pyrogram with one from a reference library. Since, in many cases, decomposition produces a pattern of peaks that are not individually identified, the resulting chromatogram is employed as a "fingerprint." Jain et al. [*121*] demonstrated the use of pyrolytic GLC for the identification of small samples of paint. Characteristic pyrograms were obtained from different types of paint vehicles and those with the same vehicles but different pigments. The method was recommended for use in the forensic field where, very often, chips or traces of paint are the only physical evidence. Groten [*122*] investigated a broad spectrum of polymeric materials and found that they all produced characteristic pyrograms. McKinney [*123*] compiled a bibliography on pyrolysis gas chromatography for the period 1960 to 1963 that includes a subject and author index. A comprehensive treatment of pyrolysis chromatography, with special reference to paint resins, was presented by Hillman [*124*]. The study included 22 pyrograms of various types of coating materials in addition to a discussion of the effects of operating conditions and polymer structure on the resulting chromatograms.

As mentioned before, alkyd resins do not yield well-defined pyrograms that can be used for compositional analysis. Pyrolysis of alkyd resins is most useful for the examination of minute chips or flakes of paint. If an adequate amount of wet sample is available, alkyd resins may be examined best by gas chromatography of the fatty and dibasic acid methyl esters [*105,111*] and the trimethylsilyl ethers of the polyhydric alcohols [*117*]. Styrenated and acrylated alkyds, however, give good yields of monomer from the modifying resin, and with proper calibration the concentration of modifying resin can be ascertained.

When the pyrolysis is limited to certain classes of resins, for example, methacrylate and polystyrene, high yields of monomer are obtained that can be equated with the copolymer composition of the polymer through the use of calibration mixtures. Since copolymers do not give the same pyrograms as physical mixtures of the same composition, physical mixtures cannot be used for the quantitative analysis of copolymers. A random rupture of bonds occurs when acrylate is pyrolyzed; yields of monomer are low, accompanied by the esterification alcohol and gases. A scheme for the identification of copolymer composition of thermosetting acrylic resins has been presented [*108*]. In this method, a filament was coated with the resin solution and dried prior to decomposition. Twelve monomers were identified by combined analysis on polar and nonpolar columns.

Plasticizers

One of the most desirable properties of a plasticizer is low volatility, and for this reason it would be expected that the analysis of such materials by GLC would not be easy. Indeed, the vapor pressures of many plasticizers are so low that they have been recommended as stationary liquid phases for GLC analysis where moderate operating temperatures are adequate. However, by a suitable choice of operating conditions, most nonpolymeric plasticizers may be chromatographed without great difficulty.

In general, reasonable emergence times of high boiling compounds may be achieved by the use of short columns, rapid flow of carrier gas, high operating temperatures, or low-liquid-phase concentration. Since each of these operating conditions can produce undesirable effects such as poor resolution, reduced column longevity, and tailing, a compromise must be reached that will allow the resolution of high boiling mixtures within a reasonable time span. A 9-in. (22.86-cm) silicone grease column [*127*] was found to be adequate for the quality control of incoming stocks of butyl benzyl phthalate. Differences in the manufacturing processes of this plasticizer leads to products of variable composition, and, although a high yield is the desired end product, appreciable amounts of dibutyl and dibenzyl phthalate are sometimes encountered. When incorporated with acrylic resins, dibutyl phthalate tends to distill out of a lacquer on exposure, a condition that may ultimately lead to resin embrittlement.

A method for the analysis of plasticizers was presented [*128*] in which a 6-ft (1.82-m) silicone grease column was used to separate a broad range of plasticizers. A rapid flow of carrier gas, 120 mL/min, and a high terminal column temperature, 290°C, were used in conjunction with temperature programming for the separation of low, medium, and high boiling plasticizers.

Miscellany

Ghanayem and Swann [*135*] separated glycols on polar columns without resorting to derivative formation. A method of this type is useful where the purity of low-boiling, uncombined polyol is under consideration. High-boiling polyols, however, normally require derivatization prior to the chromatographic step. The ever-increasing popularity of aerosol packaging has generated considerable interest in methods for the chemical analysis of aerosol propellants. The performance characteristics of various propellants may vary

over a broad range; flammability, toxicity, vapor pressure, and solvency are some of the factors that determine their usefulness. It is practically impossible to identify propellants using conventional methods; they are, however, susceptible to GLC analysis. A two-column method [*136*] has been devised for the identification of propellants in aerosol-packaged paint. In this method, a 22-ft (6.70-m) silicone grease column is used at ambient temperature for the separation of fluorinated compounds, chlorinated hydrocarbons, and aliphatic hydrocarbons. A 6-ft (1.82-m) porous polymer column is used for the separation and identification of carbon dioxide. The concentration of each propellant may be approximated from the ratios of peak heights or peak areas. Obtaining a representative sample from an aerosol can could, prior to solvent analysis, present some difficulties to inexperienced analysts. Rastogi [*137*] suggested freezing the aerosol can in liquid nitrogen, puncturing the can, and allowing the propellant to evaporate as a sample preparation method.

The many applications of GLC to paint analysis are too numerous to mention; indeed, the number is vast and continues to grow. Eiceman et al. [*138*] reviewed the fundamental developments in gas chromatography for the period 1990 and 1991 and noted the attention given to the characterization of liquid phases and prediction of retention behavior. A review of the usual methods of quantification by headspace gas chromatography for liquid samples was presented by Nagai [*139*] in 1991.

In today's laboratory environment where analysts are required to multitask, autosamplers are helpful not only for productivity reasons but also for increasing accuracy and precision. The design, operation, and troubleshooting of GC autosamplers was discussed by Hinshaw [*140*]. Moreover, the labor cost associated with troubleshooting could be prohibitive when the analytical laboratory relies solely on the GC instrument manufacturer. It is critical for the analysts to be fully informed and educated about all aspects of problem solving, including the chromatographic hardware. A paper [*141*] covering trace-level sampling, principles of splitless injection, post-injection effects, and troubleshooting splitless injection was published in 1991.

Gas-Solid Chromatography

Gas-solid chromatography (GSC) represents a gas chromatographic technique where components are separated on a solid rather than on a liquid phase. Its application to the analysis of coating materials has been extremely limited, and for this reason only a very brief description of GSC processes will be presented with special emphasis being directed to new developments and potential applications to paint analysis.

Instrumentation and interpretation of data are basically the same as in GLC, the only departure from GLC convention being the absence of a liquid stationary phase. Initially, GSC methods were used primarily for the analysis of very volatile, inert materials, but with the introduction of new packing, the technique has been extended to the analysis of a much broader spectrum of chemical types. Alumina, silica gel, molecular sieve, organoclay, and porous polymers are the most widely used GSC packing materials. GSC with silica gel, alumina, or organoclay preclude the analysis of polar solutes since polar solutes are irreversibly adsorbed on surface-active groups. Of the GSC packings mentioned, porous polymers are the most recent, and, owing to their versatility, they offer the best potential for GSC analysis of coating materials.

Porous Polymer Packings—Porous polymer beads represent a unique advance in column technology by making use of polymer synthesis to produce columns for specific applications. Porous polymer beads are derived from the same family of polymers used in gel-permeation chromatography; they were first introduced as a GC packing by Hollis [*146*], who demonstrated their application to various chemical species.

The porous polymer beads used by Hollis were prepared from styrene, *t*-butylstyrene, and ethylvinylbenzene cross-linked with divinylbenzene. By varying the monomer ratios and polymerization conditions, the properties of the polyaromatic beads can be varied with regard to chemical structure, pore structure, particle size, and surface area. Consequently, beads of different performance characteristics can be synthesized. Porous polymer beads from different sources have been studied [*147*]; their physical properties and performance characteristics have been described in great detail.

Technically, the use of porous polymer beads packings should not be classed exclusively as GSC since partition and diffusion, as well as adsorption, all contribute to their effectiveness. Most likely, adsorption predominates at low temperatures and partition at high temperatures. Porous polymer beads have good mechanical strength, which permits their being packed by conventional vibration techniques. Most beads can be used up to 250°C with little or no bleeding, and this characteristic is particularly important when high-sensitivity detectors are used in conjunction with temperature programming. Unlike diatomaceous earth packings, porous polymer beads are hydrophobic, eluting water very rapidly with little or no adsorption. The potential uses of such packings are still being explored, but excellent results have been already achieved for the analysis of polar compounds [*148*], these chemical types being difficult to chromatograph on conventional GLC columns.

Finally, the readers may find the list of ASTM practices relevant to chromatography shown in Table 5 useful in their practice of chromatography.

GAS CHROMATOGRAPHY GLOSSARY

The following definitions of terms used in GC were compiled by Brenner and Olson [*149*] and the International Union of Pure and Applied Chemistry under the Chairmanship of Dr. Ambrose [*150*].

adsorbent (active solid)—Solid, granular material used to pack columns and on the surface of which sample components are held by adsorptive forces.

adsorption chromatography—*See* **gas-solid chromatography.**

adsorption column—Column used in gas-solid adsorption chromatography. The column material consists of an active solid (adsorbent).

TABLE 5—ASTM practices relevant to chromatography.

D 2743	Practices for Uniformity of Traffic Paint Vehicle Solids by Spectroscopy and Gas Chromatography
D 3960	Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings
E 260-91	Practice for Packed-Column Gas Chromatography
E 355-77(1989)	Practice for Gas Chromatography Terms and Relationships
E 516-91	Practice for Testing Thermal Conductivity Detectors Used in Gas Chromatography
E 594-77	Practice for Testing Flame Ionization Detectors Used in Gas Chromatography
E 682-79	Practice for Liquid Chromatography Terms and Relationships
E 685-79	Practice for Testing Fixed-Wavelength Photometric Detectors Used in Liquid Chromatography
E 697-91	Practice for Use of Electron-Capture Detectors Used in Gas Chromatography
E 840-91	Practice for Using Flame Photometric Detectors in Gas Chromatography
E 1140-86	Practice for Testing Nitrogen/Phosphorous Thermionic Ionization Detectors for Use in Gas Chromatography
E 1151-87	Practice for Ion Chromatography Terms and Relationships
E 1303-89	Practice for Refractive Index Detectors Used in Liquid Chromatography

air peak—The peak of a substance that is not retarded by the column material, thus indicating the time necessary for the carrier gas to travel from the injection point to the detector.

attenuator—An electrical element containing a series of resistances that may be selected by a switch to produce the reduction of input voltage to a recorder by a fixed factor.

band—*See* **peak.**

band area—*See* **peak area.**

baseline—The line drawn by the recorder pen when no sample is being measured in the detector.

capillary column (open tubular column)—Tubing of small diameter, usually 0.25 to 1.0 mm inside diameter, in which the inner walls of the tube are used to support the stationary liquid.

carrier gas—The gas, usually inert, that constantly flows from a pressurized source through the chromatograph, impelling the sample through the system.

chromatogram—The graphic recording of the detector response versus time or volume of carrier gas.

column—A metal or glass tube packed or internally coated with the column material through which the sample and carrier gas flow and in which the chromatographic separation is performed.

column material—The material contained in the column. In adsorption chromatography, the column material is the adsorbent itself; in partition chromatography, the column material consists of a stationary phase distributed on an inert solid support or coated on the inside wall of the column.

component—A pure compound contained in the sample mixture.

detector—A measurement device, usually electrical, that emits a signal in the presence of a component that is eluted from a chromatographic column.

elution—The "washing" of a component through and out of the column by the carrier gas.

filament element—A type of thermal conductivity device in which a fine tungsten or similar wire is used as the variable resistance element in the cell chamber.

flow programming—A technique in which the carrier gas flow rate is gradually increased in order to expedite the elution of the higher boiling components.

gas chromatography (GC)—Collective noun for all chromatographic methods in which the moving phase is a gas. The term "chromatography" implies that a stationary phase is present in addition to the moving phase. These methods are also called *vapor-phase chromatography* (VPC).

gas-liquid chromatography (GLC)—Chromatographic method in which the stationary phase is a liquid distributed on a solid support. The separation is achieved by partition of the components of a sample between the phases. This method is also called *gas-liquid partition chromatography* (GLPC).

gas-solid chromatography (GSC)—Chromatographic method in which the stationary phase is an active solid (adsorbent). The separation is achieved by adsorption of the components of a sample. This method is also called *gas-solid adsorption chromatography.*

integrator—A mechanical or electromechanical device for producing a continuous summation of detector output with respect to time, yielding a measurement of included area of a chromatographic band.

ionization detectors—Chromatographic detectors in which the measurement of a sample is derived from the current produced by the ionization of sample molecules induced by thermal, radioactive, or other excitation sources.

katharometer (catharometer)—*See* **thermal conductivity cell.**

Liquid phase—A liquid that is relatively nonvolatile at the column temperature and is sorbed on the solid support where it acts as a solvent for the sample. The separation achieved differs with differences in solubility of the various components of the sample in the liquid phase. This is also called the *stationary phase* or *substrate.*

moving phase (mobile phase)—The carrier gas within the column, in which sample component molecules progress down the length of the column.

partition chromatography—*See* **gas-liquid chromatography.**

peak—The portion of the chromatogram recording the detector response while a single component emerges from the column. (If the separation of a mixed sample is incomplete, two or more components may appear as one peak.)

peak area—The included area formed by the ascending and descending arms of a chromatographic-recorded band and the baseline of the chart.

potentiometric recorder—A readout device in which a pen, whose deflection is proportional to the voltage output of the chromatographic detector, writes on a paper chart that is moving at a constant speed.

pyrolysis—A technique in which nonvolatile samples are thermally decomposed in the absence of oxygen in the inlet

system and the volatile products are admitted to the chromatographic column.

relative retention—The ratio of the retention time of a component to the retention time of a second component chosen as a standard.

resolution—The degree of separation between peaks.

retention index—The number of carbon atoms (multiplied by 100) of a hypothetical normal paraffin which under the given conditions would have a retention time identical to that of the substance of interest.

retention volume—The product of the retention time of a component and the volumetric flow rate of the carrier gas.

retention time—The elapsed time from injection of the sample to recording of the peak maximum of a component band.

sample—The gas or liquid mixture injected into the chromatograph for analysis.

sample injector—A device by which a liquid or gaseous sample is introduced into the apparatus. The sample can be introduced directly into the carrier gas stream or into a chamber temporarily isolated from the system by valves that can be changed so as to instantaneously switch the gas stream through the chamber.

separation—The elapsed time between elution of two successive components, measured on the chromatogram as the distance between the recorded bands.

solid support—The granular material upon which the thin layer of liquid in a partition column is held.

solute—The individual fractions of the sample dissolved in the liquid phase during their travel through the column. This is also used as another term for the sample itself.

solvent—Synonym for the liquid phase.

span of a recorder—The signal level (number of millivolts) required to produce a change in the deflection of the recorder pen from zero to 100% on the chart scale.

splitter—A T-fitting attached to the column to divert a portion of the flow. An *inlet splitter* allows introduction of very small samples to a capillary column. An *effluent splitter* may be used to permit parallel operation of two detectors.

stationary phase—*See* **liquid phase.**

substrate—*See* **liquid phase.**

tailing—A form of band distortion in a chromatogram in which the trailing edge returns to the baseline relatively slowly, producing an asymmetrical band.

temperature programming—A technique in which the column temperature is gradually increased in order to expedite the elution of the higher boiling components.

thermal conductivity—A physical property of materials that is the ability to conduct heat from a warmer to a cooler object.

thermal conductivity cell—A chamber in which an electrically heated element is contained that, by its change in resistance, will reflect changes in thermal conductivity within the chamber atmosphere.

thermistor bead element—A type of thermal conductivity detection device in which a small glass-coated semiconductor sphere is used as the variable resistive element in the cell chamber.

vapor-phase chromatography (VPC)—*See* **gas chromatography.**

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Electron Microscopy

by John G. Sheehan[1]

THERE ARE TWO MAIN TYPES of electron microscopes, the scanning electron microscope (SEM) and the transmission electron microscope (TEM). Today both SEM and TEM are used for microstructural examination in nearly all disciplines of science and engineering. The resolving power of electron microscopes is three orders of magnitude greater then light-optical microscopes. Modern SEMs with field-emission electron guns resolve better than 1 nm, and modern TEMs resolve better than 0.2 nm [*1*]. Contrast develops in SEM by electrons emitted at or near the surfaces of bulk specimens and therefore topography and composition are examined. Contrast develops in TEM by electrons transmitted through thin specimens and therefore variations in structure and composition are examined.

Types of signals generated in a sample of varying thickness by incident electron beam are illustrated in Fig. 1. The SEM collects secondary electrons (SE), backscatter electrons (BE), and X-rays from surfaces of bulk specimens. The TEM collects X-rays, elastically scattered electrons, and inelastically scattered electrons from thin and ultra-thin specimens. Hybrid TEMs have SEM capabilities: they collect BE that exit the incident-beam side of thin specimens, and they collect SE and X-rays from both sides. These are known as scanning transmission electron microscopes (STEM) or analytical electron microscopes (AEM).

SEM and TEM were both invented in the 1930s in Germany. TEM quickly became widely used to image replicas of surfaces at resolution far better than was possible with the first SEM and therefore further attempts to develop SEM were regarded as a waste of time. SEM did not become available commercially until 1965, when Cambridge Instrument Company marketed the "Stereoscan" [*2*]. Immediately SEM became widely used to examine coatings, as seen in American Chemical Society Symposia on SEM of coatings in 1968 [*3*] and again in 1972 [*4*]. Today the higher resolution available from SEMs has mostly replaced TEM of surface replicas, since TEM is no longer needed to see sub-micrometer pigment and latex particles. Therefore SEM will receive most of the attention in this chapter.

This chapter has three main parts: SEM, TEM, and applications to coatings. The SEM section begins with a discussion of image formation and signal collection; these must be understood to correctly interpret SEM images. Then, the electron-optical column that includes the electron gun, the condenser lens system, the scan coils, and the objective lens are discussed. The function of each must be understood in order to create ideal conditions for SEM imaging. Also included is a discussion of X-ray microanalysis, used to identify qualitatively or quantitatively the elements present in a sample. The SEM section ends with a discussion of metal coating, needed to prevent charge buildup on nonelectrically conductive samples during SEM imaging. As resolution of SEM has improved, it has become critical to coat samples with ultra-thin films (1 to 5 nm) that do not blanket surface details to be imaged.

The TEM section has a brief discussion of contrast and electron optics. The last section discusses some of the wide range of applications of electron microscopy to coatings, from practical problems of identifying contaminants, to fundamental research of latex coalescence and adhesion.

SCANNING ELECTRON MICROSCOPY

The scanning electron microscope (SEM) images surfaces at magnifications from about ×10 to ×200 000. Depth of focus is large, so rough surfaces can be imaged. The types of signals that can be collected include secondary electrons (SE), backscatter electrons (BE), and characteristic X-rays. An image of a sample in the SEM is formed on a cathode ray tube (CRT) by a dot-mapping process. As the electron beam scans the sample, the signal from each spot is collected, amplified, and synchronously displayed on the CRT with an intensity proportional to the collected signal. The same scan generator deflects the electron beam across both the sample and the CRT and therefore the signal displayed on the CRT is a magnified image of the scanned area.

A schematic diagram of the SEM is shown in Fig. 2. Electrons are pulled out of the gun by the electric field between the gun and the anode. The condenser lenses form the beam into a finely focused probe. The scan coils cause the probe to scan across the sample in a raster. The objective lens focuses the beam on the sample. Any combination of BE, SE, and characteristic X-rays can be detected. Details of the function of each component in the SEM are discussed below.

Image Formation

Most SEMs are equipped to detect secondary electrons (SE), backscatter electrons (BE), and characteristic X-rays as the electron beam scans across sample surfaces. The SE signal is produced when bound electrons are removed as a result of inelastic scattering of the electron beam. The intensity of

[1]Unilever Research, 45 River Road, Edgewater, NJ 07020.

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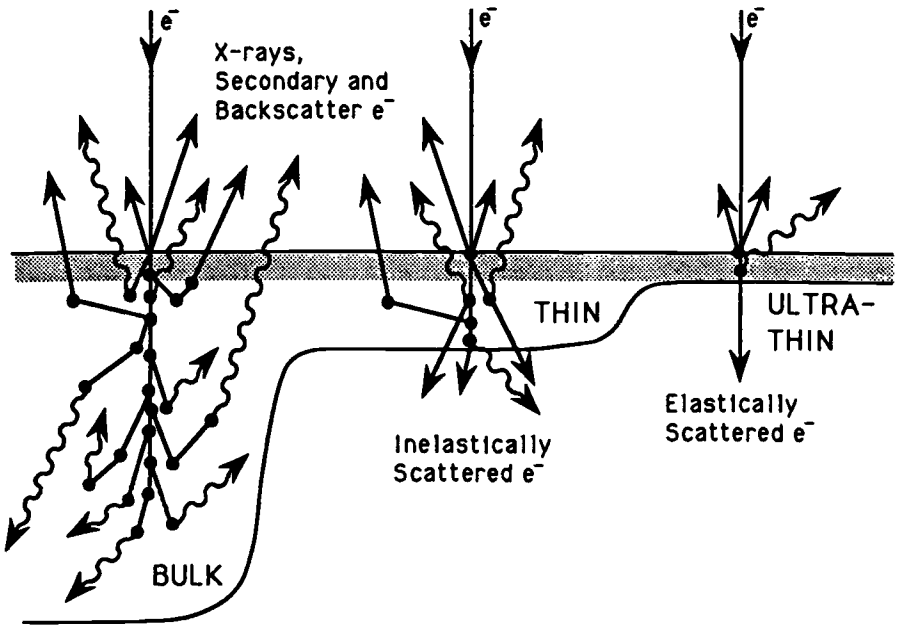

FIG. 1–Signal types generated by electron beams impinging on a sample of varying thickness. Adapted from Thomas [*1*].

the SE signal depends partly on the orientation of the sample with respect to the electron beam, which is why SE images are topographical.

Backscatter electrons (BE) result from elastic scattering. Electrons are elastically scattered when they penetrate the electron clouds of atoms and change direction, a result of coulombic interaction with the positively charged nuclei, known as Rutherford scattering. An electron is backscattered after a series of direction-changing elastic events that cause the electron to exit the sample. The probability of a backscatter event depends on the size of the nuclei and therefore backscatter contrast depends on the distribution of average atomic number in the sample. The depth in a sample from which BE information emerges ranges from about 80 nm for gold to about 600 nm for aluminum with an accelerating potential of 20 kV [*6*]. The yield of BE varies by only about 10% over an accelerating-potential range of 10 to 50 kV [*5*].

Most SEM images are collected with the Everhart-Thornley (ET) detector, shown in Fig. 3. The ET detector collects mostly SE and some BE. The main components of the ET detector are a collector grid, a scintillator, and a photomultiplier. SEs, whose average energy is about 3 to 5 eV [*5*], are pulled toward the scintillator by a 300-V potential on the collector grid. A 10-kV bias on the scintillator accelerates SEs enough to cause photon emission in the light pipe. The collection grid also protects the electron beam from deflection by the 10-kV bias on the scintillator.

Secondary electrons are classified into four types, shown schematically in Fig. 3. SE-1 are generated by direct interaction with the primary beam and therefore carry the highest resolution information. SE-2 are generated by backscatter electrons as they exit the sample surface and therefore generate sub-surface atomic number contrast. In 1940, before the first SEM images were collected, von Ardenne correctly predicted that SE-2 would limit resolution: SE-2 cannot be detected separately from SE-1. McMullan [*2*] wrote an historical account.

SE-3 are generated by backscatter electrons that strike the objective lens pole piece and the specimen chamber walls. SE-4 are generated when the primary beam strikes pole pieces and apertures. SE-3 generated at the objective lens pole piece can be reduced with a shield made of low SE-emitting material, such as carbon-coated aluminum, placed just below the objective lens. A +50-V bias, applied to the shield, also prevents escape from the shield of any SE-3. To increase atomic number contrast, BEs that strike the shield can be converted into SEs when the shield is positively biased or covered with a material that emits a large number of secondary electrons. Reimer [*6*] discussed signal types in detail. Peters [*7*] discussed high-resolution SE image formation.

There are two main types of BE detectors. One is the ET detector described above, an inefficient way to collect BE: the geometric collection efficiency of BE in an ET detector is only about 1 to 10% [*5*]. The efficiency is low because most BEs travel away from the sample in the beam direction, and ET detectors are usually mounted away from the beam axis. Collection efficiency is improved if a disk-shaped detector is placed at the bottom of the objective lens, with a hole in the middle for the electron beam. Both solid-state and scintillation-type detectors are used in this way.

To demonstrate the importance of understanding how SE1, SE2, SE3, and BE generate contrast in the SEM, three micrographs of the same area of a 1:6 styrene-butadiene latex:calcium carbonate coating formulation, air-dried from 80 wt%, are shown in Fig. 4. Micrographs in Figs. 4A and 4B were recorded at 20 and 5 kV, respectively, with an ET detector. In Fig. 4A, the calcium carbonate particles are visible from beneath the latex-film surface from a combination of SE-2, SE-3, and BE.

This is possible because the exit depth of BE from a latex film is about 1 μm at 20 kV. In Fig. 4B, the calcium carbonate

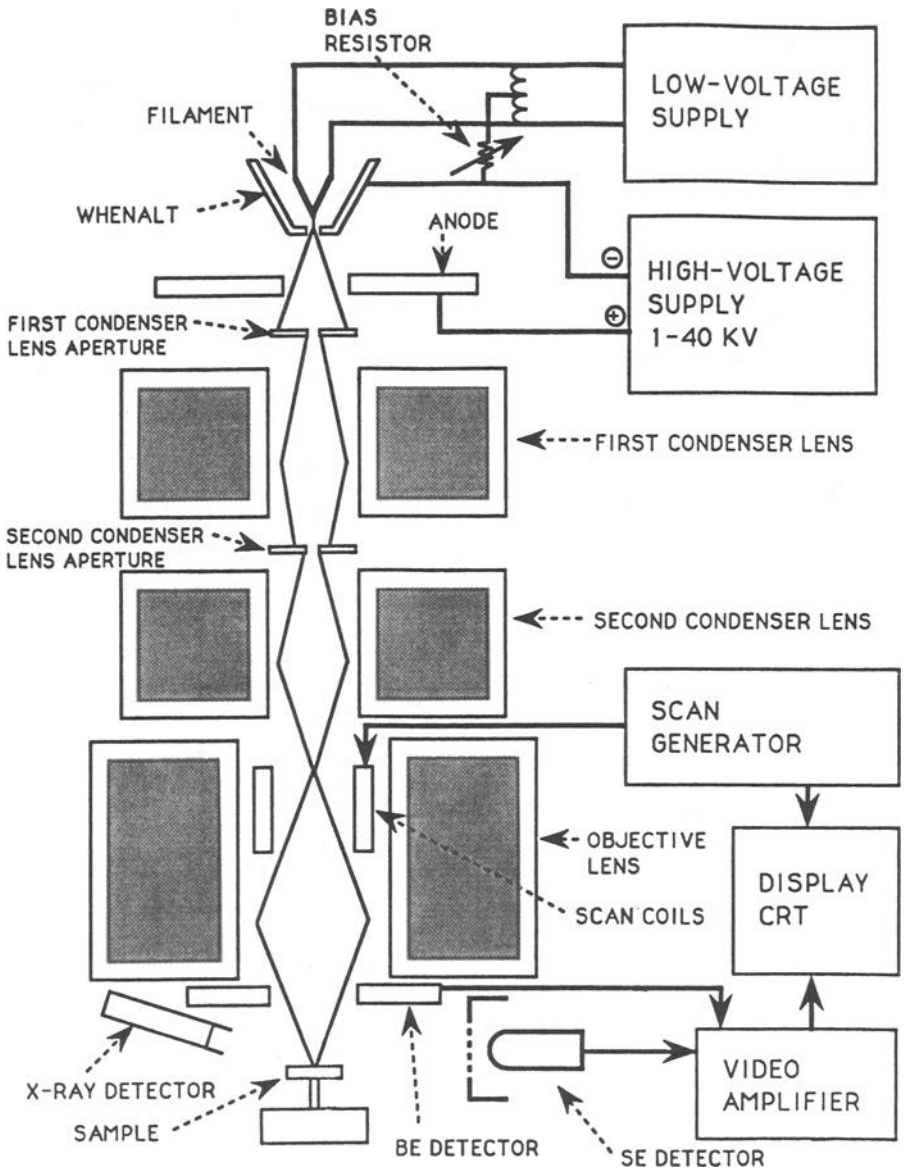

FIG. 2–Schematic diagram of an SEM with a thermionic electron gun. Adapted from Thomas [1].

particles are barely visible because the exit depth of BE, and therefore contrast from SE-2 and SE-3, is less than 100 nm at 5 kV. Comparison of Figs. 4A and 4B demonstrates the strong dependence of accelerating voltage on the appearance of SEM images: sometimes more than one accelerating voltage is needed for correct interpretation. Also, SE images at lower accelerating voltage better represent topography because the exit depth of BE is smaller.

The micrograph in Fig. 4C shows the same area as Figs. 4A and 4B, this time recorded with an annular solid-state BE detector that was attached to the bottom of the objective lens. Because no SEs were detected, the latex binder at the sample surface generated no contrast. Instead, contrast was generated by the distribution of calcium carbonate particles beneath the latex-film surface. This example illustrates the importance of understanding image formation in the SEM in order to correctly interpret images. Observation of only Fig. 4A would lead one to the false conclusion that the latex film does not cover all of the calcium carbonate particles.

X-Ray Microanalysis

Inner shell ionization is the event that triggers characteristic X-ray production. An X-ray photon is produced when an electron from an adjacent shell drops to an inner shell to replace the ionized electron. Each element has its own set of characteristic X-rays and therefore elements present in a sample can be identified qualitatively or quantitatively if a spectrum of emitted X-rays is collected.

There are two types of X-ray detectors, the wavelength dispersive spectrometer (WDS) and the energy dispersive spectrometer (EDS). In WDS, a small portion of the emitted X-rays hit a crystal. X-rays that satisfy Bragg's law for the crystal are diffracted to a proportional counter. X-ray spectra

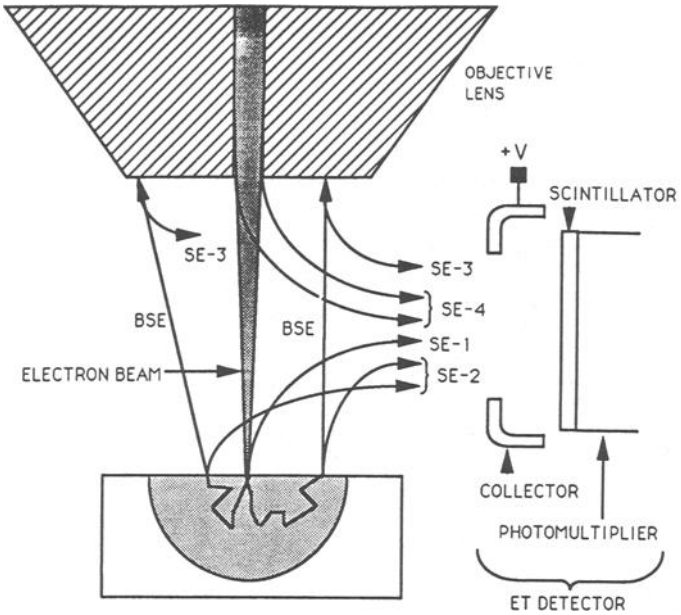

FIG. 3–Types of secondary electrons collected by the Everhart-Thornley detector. SE-1 carries high-resolution information, but it cannot be separated from SE-2. Adapted from Reimer [*6*].

are collected by varying the crystal angle. The advantage of WDS is high-energy resolution, 6 to 30 eV.

Before 1968, when EDS was introduced, all X-ray microanalysis was done with wavelength-dispersive spectrometers. Today, EDS is installed on most SEMs. In EDS, X-rays pass through a thin (ca 8-μm) beryllium window into a lithium-doped silicon detector. The energy of incoming X-rays is measured from the number of electron-hole pairs generated in the silicon detector. The beryllium window separates the vacuum in the microscope from the crystal. The crystal is cooled with liquid nitrogen to reduce the leakage current. Low energy resolution (about 150 eV) is the disadvantage of EDS compared to WDS. However, the whole energy spectrum in EDS can be recorded simultaneously and therefore elements in a sample can be quickly identified. The detection limit of an Si(Li) detector with a beryllium window is down to $Z = 11$ (Na). Windowless and ultra-thin window detectors extend the detection range down to $Z = 4$ (Be).

In quantitative X-ray analysis with EDS, the X-ray intensities of each element in a sample are measured and compared to the measured intensities of pure-element standards. The concentration of each element in the sample is the ratio of the X-ray intensity of each element in the sample to that in the standard. However, corrections are needed to account for the different ways X-rays are generated in the sample compared to the standard. These include backscattering and the stopping power (Z), X-ray absorption (A), and fluorescence (F). Together, these corrections are known as the ZAF correction. All EDS spectrometers available from commercial vendors have computer programs that calculate ZAF corrections. More on quantitative X-ray microanalysis is found in Refs *5* and *6*.

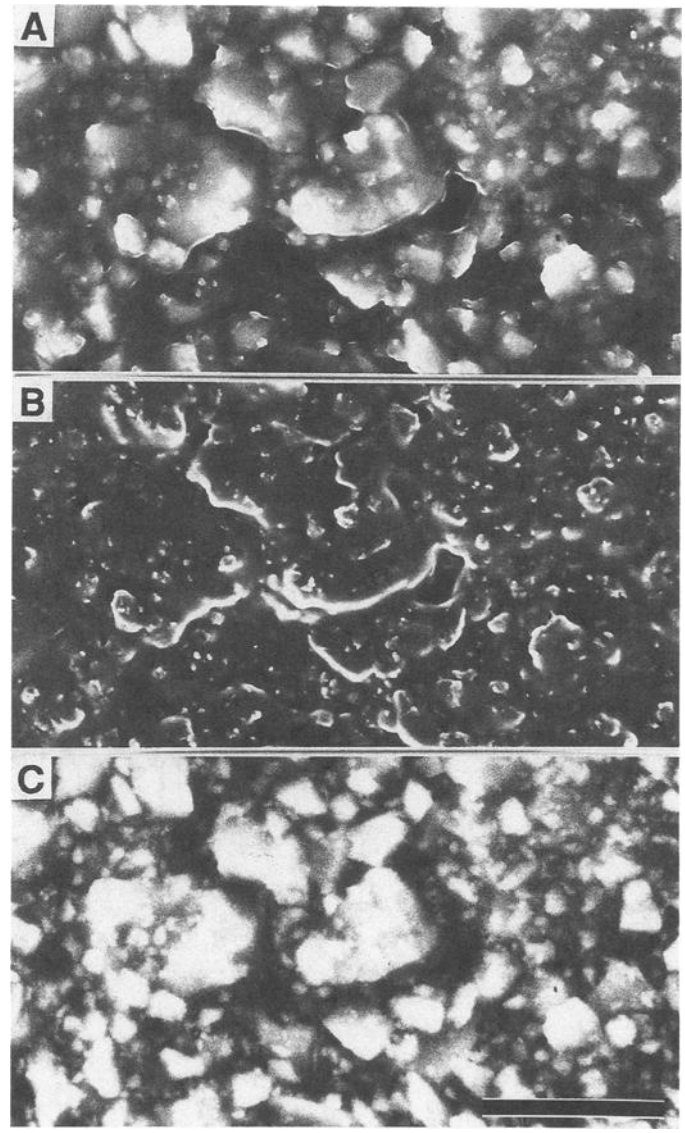

FIG. 4–Three SEM images of the same area of a coating formulation with 1:6 latex:calcium carbonate, air dried from 80 wt% aqueous suspension. (A) SE image at 20 kV; (B) SE image at 5 kV; (C) BE image at 20 kV. Bar = 10 μm.

Electron Guns

The ultimate resolution of an SEM is determined by the type of cathode in its electron gun. The main measures of electron gun performance are current density and diameter of the first crossover. High current density and a small first crossover are needed for high-resolution imaging.

There are two types of cathodes, thermionic and field emission (FE). Thermionic excitation occurs when a filament is heated to near its melting point, allowing electrons to overcome their work function and eject themselves into the vacuum. Tungsten and lanthanum hexaboride (LaB_6) are the most common thermionic cathode materials. Tungsten cathodes consist of a wire bent like a hairpin. They are easy to operate, and moderate vacuum prevents oxidation (1 to 5 $\times$ 10^{-3} Pa). However, they require frequent replacement: every 2 to 40 h. LaB_6 cathodes consist of a crystal of the material,

usually soldered to refractory metal strips. One advantage of LaB_6 over tungsten is its higher current density, 20 to 50 A/cm^2, compared to tungsten at about 3 A/cm^2. Another is the smaller diameter of the first crossover, about 10 μm for LaB_6 and 50 μm for a tungsten hairpin. Together, these make the resolution of LaB_6-equipped SEMs higher. Another advantage of LaB_6 cathodes is their longer lifetimes, 200 h or more. However, LaB_6 guns require more frequent and more precise alignment than tungsten guns. Better vacuum ($<10^{-4}$ Pa) is required to slow evaporation that results from reactions of LaB_6 material with oxygen-containing residual gases [*6*].

Field emission occurs when a huge potential gradient ($>10^7$ V/m) is applied to a tungsten tip of about 0.1 μm in diameter, causing electrons to tunnel through their potential barrier. No thermal energy is needed to lift the electrons over the barrier. The combination of high current density and small diameter of the first crossover in FE guns makes possible ultra-high resolution (<1 nm) SEM imaging, not possible with thermionic cathodes. The current density is around 10^6 A/cm^2, three orders of magnitude greater than LaB_6 cathodes. The diameter of the first crossover from a field emitter is only about 10 nm and therefore only one condenser lens is needed to demagnify the probe enough for high-resolution imaging. Gas molecules that strike the tip cause the work function to rise and the emission to fall. Field emitters that operate at room temperature (known as "cold-field" emitters) require vacuum better than 10^{-8} Pa. Even in a clean vacuum, gas molecules eventually cover the tip. The tip is cleaned by rapid heating to around 2300 K. Field emitters that operate at around 1200 K are less susceptible to gas molecules, and field-emission is stable at pressures up to 10^{-7} Pa [*6*].

SEM at low accelerating voltages (1 to 5 kV) has advantages of high topographic contrast, less specimen damage, and less surface-charge buildup. Until recently, low-voltage SEM was limited in resolution mainly by large chromatic aberrations in objective lenses, which arise from the large energy spread of electron beams from thermionic cathodes. This problem has been overcome by FE cathodes, whose energy spread is more than ten times smaller than in thermionic cathodes. The merits of low-voltage SEM with FE cathodes were discussed by Pawley [*8*].

Condenser Lenses, Scan Coils, and Objective Lenses

The purpose of the condenser lens system in the SEM is to deliver electrons from the first crossover to the specimen plane in a small-diameter, high-intensity beam. SEMs with thermionic electron guns have two condenser lenses, as shown in Fig. 2. Each condenser lens and spray aperture demagnifies the probe. The first condenser is placed halfway between the second condenser and the electron gun, and the second is placed halfway between the gun and the specimen. Two condenser lenses instead of one are advantageous because more electrons are collected and focused into the probe, and the probe diameter is smaller. The spray aperture in each condenser lens intercepts scattered electrons and decreases spherical aberrations. The first spray aperture is usually fixed, and the second is selectable to varying diameters. A small final probe diameter is not always advantageous because it makes small both the probe current and the signal-to-noise ratio. Higher probe currents are needed for EDS and some backscatter detectors. The operator must decide which combination of aperture and condenser lens currents fits the requirements of resolution and signal detection. Many modern SEMs do not have an aperture in the objective lens, and therefore the second condenser aperture is often called an "objective" aperture because it is the aperture closest to the sample. This can be a source of confusion because textbooks on SEM call the final aperture in the objective lens the "objective" aperture.

The scan coils deflect the electron beam across the sample in a raster. Magnification is the ratio of the CRT width to the raster width. The probe is focused at the sample surface by the objective lens. The distance between the objective aperture and the sample is known as the "working distance." The depth of focus is inversely proportional to the working distance. But probe diameters are small when the beam is focused at short working distances. So high-magnification imaging should be done at short working distances, and low-magnification imaging should be done at long working distances, where depth of focus is high.

Metal Coating for SEM

Metal coating of non-electrically conductive samples for SEM examination is required to prevent charge buildup during imaging, and metal coating increases the SE yield of non-electrically conductive samples. Coatings should be thinner than the size of the smallest surface details to be imaged. It is often written that sample preparation for SEM is "easy." However, great care is required to coat samples with ultra-thin (<5 nm) continuous films needed in order to take advantage of the high resolution now available from LaB_6 and FE-equipped SEMs.

Metal coating is best explained by theories of nucleation and growth [*9*]. During nucleation, metal atoms strike the sample surface and diffuse until they find a nucleation site, often a surface inhomogeneity, where it is energetically favorable for them to stick. Grains grow at each nucleation site as atoms arrive by either surface diffusion or direct impingement. As growth continues, adjacent grains touch and eventually begin to coalesce. When enough of the grains have touched, the film becomes electrically continuous. The area density of nucleation sites determines the size of grains required to form a continuous film. When there are few nucleation sites, grains must grow large in order to form a continuous film. When there are many nucleation sites, tiny grains grow together and form a continuous film. The strategy of ultra-thin (<5 nm) coating for high-resolution SEM is to increase the area density of nucleation sites, so that thinner, continuous films are formed with smaller grains.

Coating techniques for SEM include thermal evaporation, d-c plasma sputtering, and ion beam sputtering. Films are formed by thermal evaporation when metal is heated to its melting point in a high vacuum ($<10^{-3}$ Pa). Films formed by thermal evaporation have large grains compared to other techniques, but grain size decreases with decreasing substrate temperature [*10*]. Thermal evaporation of gold quickly became the standard coating technique when SEMs first became widely available in the late 1960s. But as the resolution of SEMs improved, the grain size of metal coatings became a limit to resolution. Coating techniques that produce thinner,

continuous films with smaller grains were needed. D-c magnetron sputtering is one of them.

In d-c magnetron sputtering, films are formed when ionized, inert gas atoms strike a metal cathode to eject metal atoms, which strike the sample. Ionization efficiencies and, hence, sputtering rates are increased with an annular magnetic field that surrounds the cathode to concentrate electrons in the cathode area [*11*]. Films made with d-c magnetron sputtering have smaller grains than thermally evaporated films. However, grain size is sensitive to contamination [*12*], and artifacts are often present [*13*]. The d-c magnetron coater is now standard equipment in the SEM lab. Many models are available and prices vary widely. Inexpensive models are evacuated with rotary mechanical pumps. Care should be taken not to allow rotary-pumped coaters to reach their ultimate pressure, otherwise pump oil can disrupt nucleation when it contaminates the target and the sample. State-of-the-art magnetron coaters are evacuated with oil-free turbomolecular pumps and equipped with cold stages because low sample temperatures promote nucleation.

A more recent development in metal coating for high-resolution SEM is ion beam sputtering. Films are formed by ion beam sputtering when a collimated ion beam strikes a metal target to eject metal atoms [*14*]. Mean grain sizes of 1 nm have been obtained for both gold and platinum [*15*], too small to be resolved with SEM. Dislodged metal atoms have about 100 eV of kinetic energy. It is speculated that high kinetic energy metal atoms implant themselves into sample surfaces, causing increased nucleation density and small grains. Ion beam sputtering is becoming widely used for ultra-high resolution SEM.

Metal film thickness should be measured to insure that only enough metal is deposited on the sample to form a continuous film. The quartz microbalance is the most widely used instrument to measure film thickness on electron microscopy specimens. Film thickness sensitivity is equivalent to about 0.05 nm of gold. Methods of film-thickness determination were discussed by Flood [*16*].

Cryogenic SEM

Conventional electron microscopes have a vacuum better than 10^{-3} Pa in their specimen chambers. This limits conventional SEM to dry samples. When volatile samples like paints are placed in the SEM specimen chamber, their solvents quickly evaporate, damage the vacuum pumps, and cause the electron beam to scatter. One solution is to lower vapor pressures by freezing and examine samples in an SEM equipped with a stage cooled by liquid nitrogen. The technique is known as cryogenic SEM (cryo-SEM), described by Sheehan [*17-19*] for examining paper-coating formulations. The reader is also referred to Echlin [*20*] for more on techniques of cryo-electron microscopy.

The procedure of cryo-SEM is to fast-freeze each sample and transfer it into a vacuum chamber attached to the SEM specimen chamber. There each sample is fractured, sometimes etched, and then coated with a thin metal film. Then each sample is transferred to the cold stage in the SEM. The challenges of high-resolution cryo-SEM are to freeze fast enough to prevent noticeable growth of ice crystals, transfer without condensing water vapor on the fracture surfaces, coat frozen-hydrated samples with an ultra-thin, continuous metal film, and image in the SEM without too much buildup of contaminants.

Wet microstructures of coating formulations can be examined with cryo-SEM after freezing and fracturing. Complementary fracture faces of a frozen-fractured pigment/latex coating formulation are shown in Fig. 5. Kaolin and calcium carbonate particles can be identified by their morphologies. The dark areas between the particles are ice. Close examination of the complementary faces shows that fracture propagated around the pigment particles.

The stages of drying can be fixed by freezing and examining with cryo-SEM. A cross section of a fractured drop of a 20 wt% aqueous suspension of styrene-butadiene latex is shown in Fig. 6. The drop was placed on a glass slide, air-dried for 3 min, and plunge-frozen into liquid ethane. The lower part of

FIG. 5–Cryo-SEM image of complementary fracture faces of a coating formulation. Bar = 1 μm [*18*].

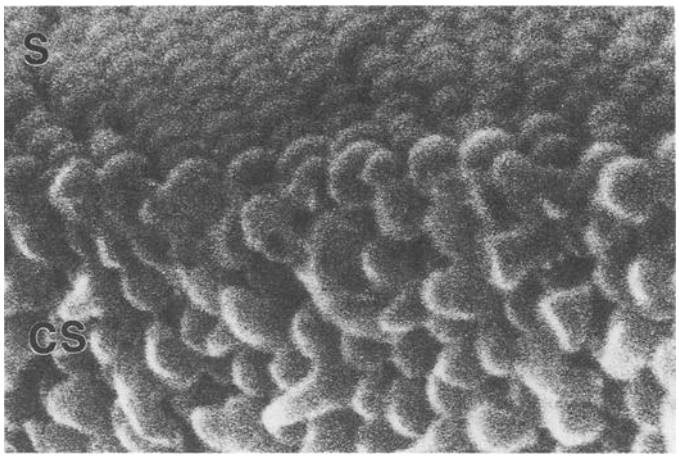

FIG. 6–Cross section of a partly dried drop of styrene-butadiene latex. The lower part (CS) is the cross section, and the upper part (S) is the drop's surface. Bar = 1 μm.

Fig. 6 is the cross section (CS), and the upper part is the drop's surface (S) that was exposed to air during drying. Latex that was deformed during fracture is seen on the cross section. Hexagonal close packing of latex is seen on the surface.

Environmental Scanning Electron Microscopy

Cryo-techniques are one way to image volatile samples in the SEM. A recent breakthrough in SEM that allows imaging of wet, volatile specimens without freezing is known as environmental SEM (ESEM) [*21*]. In ESEM, samples are imaged in a gaseous environment at pressures up to 2.7 kPa. This is made possible by a combination of a differentially pumped vacuum system, small travel distances for the electron beam in high-pressure gas, and a new biased specimen current detector known as a gaseous detector device (GSD). The gas in the specimen chamber is a medium for SE signal multiplication, and it neutralizes charge buildup on samples. Therefore, metal coating is not required for electrically insulating samples. Ultimate resolution is near that for a conventional SEM, about 5 nm. But one cannot expect this resolution from electrically insulating samples without metal coating because SE contrast is low from electrical insulators in ESEM.

The main advantage of ESEM compared to conventional SEM is that hydrated samples can be examined at saturated vapor pressures of water. This makes accessible dynamic imaging of wetting and drying by controlling sample temperature and water-vapor pressure. An ESEM image of dry paper, taken in 800 Pa of water vapor at 20°C, is shown in Fig. 7*A*. Water was condensed on the same area by raising water-vapor pressure to 1.3 kPa and lowering sample temperature to 12°C. An image is shown in Fig. 7*B*. Most of the fibers are covered with water.

Care must be taken during ESEM of hydrated specimens to avoid specimen damage by radiolysis products of water. Water molecules are radiolyzed by the electron beam into mainly hydrogen and hydroxyl radicals, which diffuse into specimens and sometimes damage them [*22-24*].

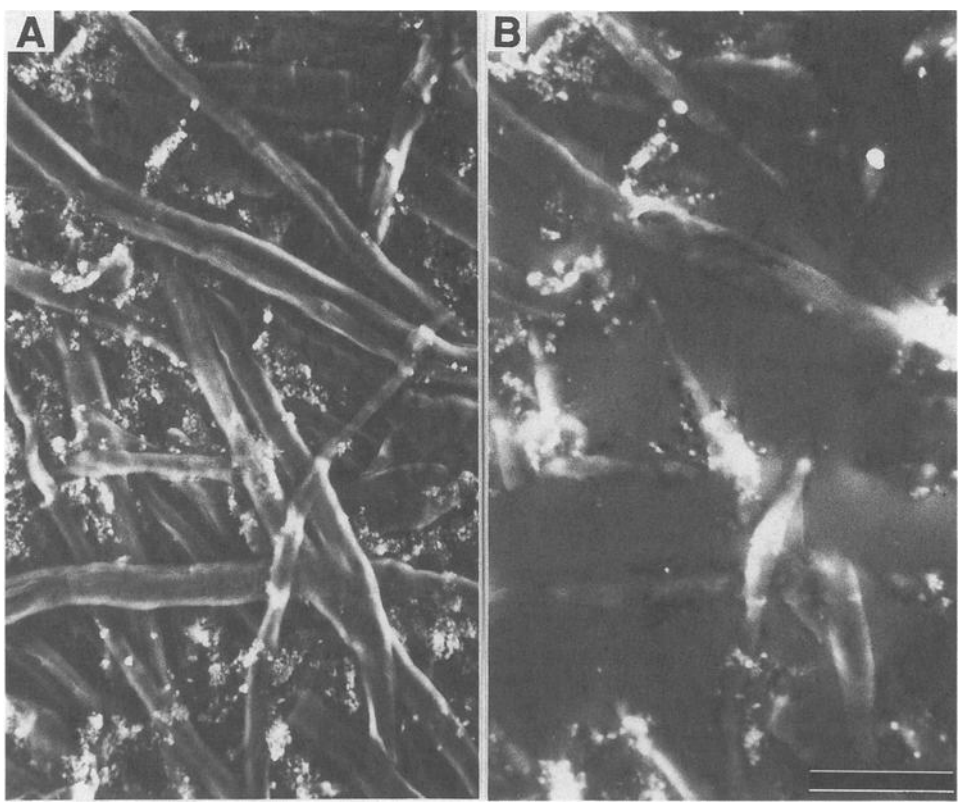

FIG. 7–Two ESEM micrographs of the same area of paper (A) before wetting; (B) wet. Bar = 50 μm.

TRANSMISSION ELECTRON MICROSCOPY

The TEM produces images from electrons that transmit themselves through thin and ultra-thin samples, as shown in Fig. 1. High-resolution TEMs resolve better than 0.2 nm. Types of contrast include scattering, diffraction, and phase contrast. The maximum useful thickness of amorphous samples at 100 kV is 100 to 3000 nm. The maximum useful thickness of metal foils and crystalline materials at 100 kV is 50 to 200 nm [*25*].

Types of Contrast

Electron beam-specimen interactions in thin and ultra-thin samples that lead to contrast in the TEM are shown in Fig. 1. Electrons are elastically scattered by coulombic interactions with positively charged nuclei as they travel through TEM specimens. Scattering contrast is also known as mass-thickness contrast because the amount of scattering depends on specimen thickness and atomic number. Scattering contrast in TEM can be imaged in the bright-field mode and in the dark-field mode. In the bright-field mode, electrons that are scattered at larger angles are intercepted by the objective aperture. Others pass through the objective aperture and form the image. In the dark-field mode, only the electrons that are scattered at large angles are used to form the image. This is accomplished by tilting the electron beam off axis or by moving the objective aperture off axis.

Another type of contrast caused by elastic scattering is known as phase contrast, the result of interference between the scattered and the unscattered electrons. Phase contrast varies as the objective lens focus is varied above or below the specimen.

Diffraction contrast results when Bragg reflections from crystalline planes interfere with the primary beam. The interference image gives information about crystal structures.

Inelastic interactions in TEM are plasmon excitations and inner-shell ionizations. Some TEMs are equipped with electron spectrometers that measure the energy loss spectrum, known as electron energy loss spectroscopy (EELS). Electronic structures are indicated by plasmon losses, whose energies are less than 50 eV. Chemical compositions are indicated by losses from inner shell (K, L, and M) ionizations [*25*].

Optics

A schematic of an electron-optical column of a TEM is shown in Fig. 8. The electron-optical column of the TEM differs from the SEM in several ways. First, the electron beam is not scanned across the sample. Instead, the condenser lens system illuminates the entire area to be imaged and a set of projector lenses beneath the sample focus the transmitted electrons on a phosphor screen, where the image can be viewed. This points to the second major difference: the purpose of the condenser lens system is not to produce a finely focused probe at the sample, as in SEM. Instead, the condenser lens system in TEM illuminates the entire area of interest with the highest electron density that will not damage the sample. Third, the TEM has a projector lens system, making imaging more difficult than in SEM. Fourth, higher accelerating potentials (100 to 1000 kV) in TEM are needed to transmit electrons through thin samples. Accelerating potentials in SEM range from about 800 V up to 40 kV.

In most imaging modes, Condenser Lens 2 is excited and Condenser Lens 1 is shut off. However, both condenser lenses are excited in TEM scanning modes, where a finely focused probe is required.

The purpose of the projector lens system is to project the transmitted electrons into an image on the phosphor viewing screen or photographic emulsion. Magnification is set by the objective lens. The objective aperture blocks scattered electrons in the bright-field mode, discussed above. Contrast is increased if a small objective is selected, but a large objective aperture is needed for high-resolution imaging.

APPLICATIONS TO COATINGS

Film Thickness Measurements

Film thickness measurement requires cross sections. There are several ways to cross-section a dried coating. The simplest is to cut by hand with a razor blade. However, the cross section will be smoother if the cut is with a microtome equipped with a diamond knife. Cross sections of coated paper are made with a microtome after embedding the paper in epoxy [*26*]. A BE image of microtome-sectioned, coated paper is shown in Fig. 9. The coating appears lighter than the fibers because of its greater average atomic number.

ASTM Test Method for Microscopic Measurement of Dry Film Thickness of Coatings on Wood Products (D 2691) states that the specimen may be sliced with a microtome or a razor blade. Whitehead [*27*] pointed out that brittle paint films can be shattered when cut with a microtome. Also, the diamond knife in a microtome is easily damaged by hard paint films. Grinding and polishing of epoxy-embedded specimens is one solution.

Failures and Defects

Pits, cracks, and loss of adhesion can be readily examined with SEM. Some contaminants can be identified by their morphologies and others by their characteristic X-rays. Here are some examples: SEM examination of a paint film that failed rapidly in a salt spray test revealed a textured surface that rusted rapidly in the pitted areas. When the paint was applied with a smooth finish, it passed the salt spray test. Poor scrubbability in a latex paint was due to lack of coalescence, readily apparent after SEM examination revealed many cracks in the film. Loss of adhesion on metal reflectors was due to insect eggs which pulled the paint off as the eggs dried. A glossy varnish which turned out flat was found to be laden with diatomaceous earth from a broken filter [*28*].

Labana and Wheeler [*29*] mapped the distributions of ions in a corroding metal-coating interface of painted phosphated steel. Ion distributions were mapped quantitatively by electron microprobe analysis equipped with wavelength dispersive detectors.

Quach [*30*] used SEM with an EDS to identify contaminants responsible for adhesive failures. Welding splatter was identified as a cause of chipping of paint on a steel building

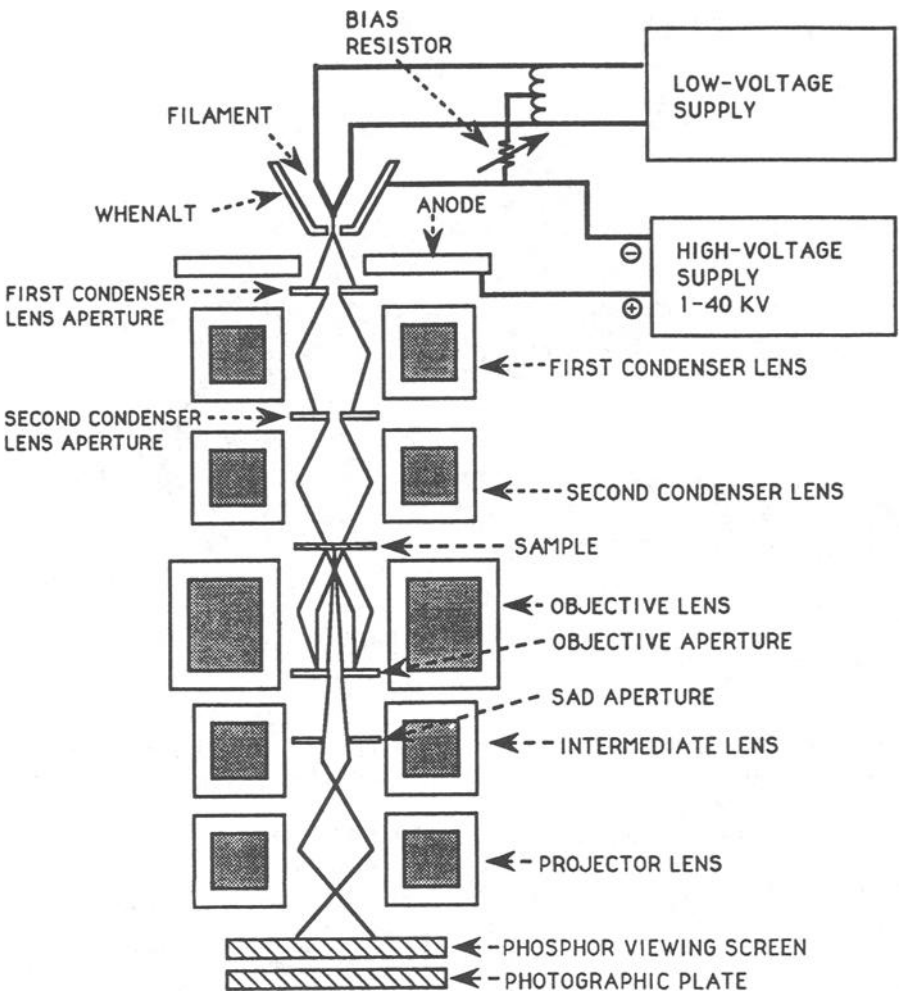

FIG. 8–Electron-optical column of the TEM. Adapted from Thomas [*1*].

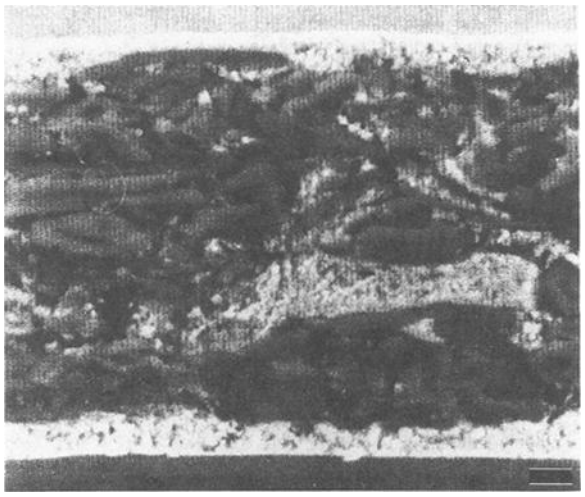

FIG. 9–Microtome-sectioned paper showing thickness of the coating and its penetration into the sheet. Bar = 10 μm. From H. Matsubayashi [*26*].

chord. It was also shown that the EDS identified plaster dust, fly ash, and SO_2 as contaminants that caused adhesive failure in other samples.

Identification of Pigments

Pigments of known morphologies can be identified easily with both SEM and TEM. Some pigment particles are smaller than 0.1 μm and therefore metal coatings must be ultra-thin in order not to blanket morphologies of the particles before SEM imaging. Pigment particles can also be identified in SEM by their EDS spectra if the particles are larger than a few micrometers. Identification of smaller particles in SEM with an EDS is hampered by the large generation volume of X-rays.

Figure 10 shows images of kaolin clay taken with SEM (10A) and TEM (10B). The different contrasts in the SE mode with the SEM and in the bright-field mode with TEM are clear. The SE contrast is topographical, and the TEM contrast depends on mass-thickness. In both, the hexagonal, plate-like habits of particles are indicators of the presence of kaolin.

Pigment Particle Sizing

The microscope is the best and also the most tedious method of determining the particle size of pigments. Other methods do not provide information of the individual shapes of the particles and sometimes give only an average particle

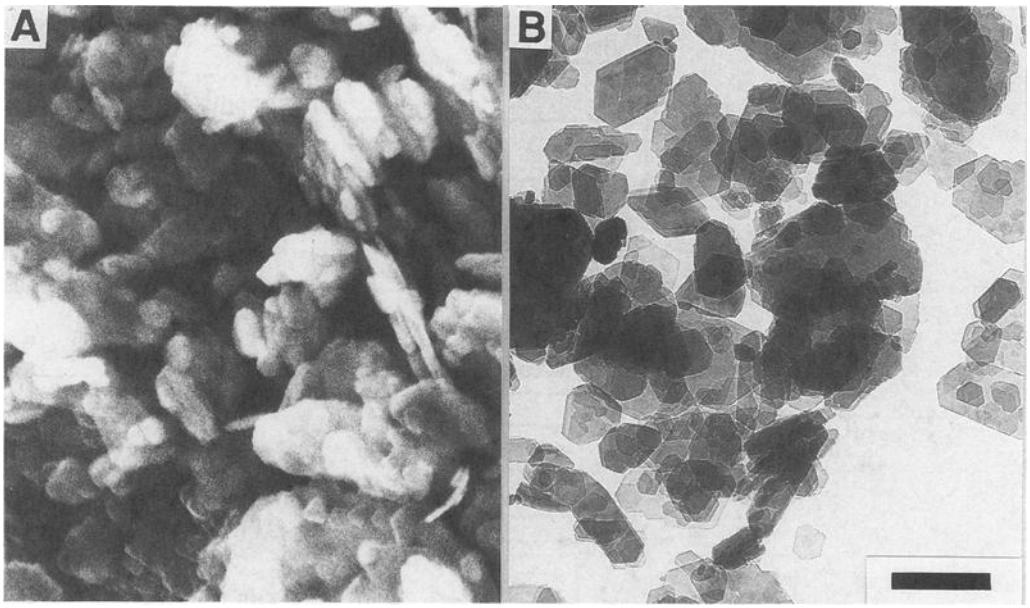

FIG. 10–Kaolin clay imaged in (A) SEM; (B) TEM. Bar = 0.5 μm. Photo by R. P. Gursky.

size without regard to size distribution. The microscope is especially useful for measurement of plate-like and needle-shape particles that do not obey Stoke's law on which the sedimentation methods are based. However, microscopic methods are slow and laborious, a disadvantage [*28*].

In the past, particle-size analysis was made by manually recording particles with the aid of a reticle. The reticle is an aid to manually counting the number of particles in each size class. However, techniques of computer-aided image processing can eliminate tedious, manual counting of hundreds or even thousands of particles.

Structure of Antifouling Paint Films

Bishop and Silva [*31*] examined leaching of pigment in cross sections of anti-fouling paint films. Cross sections were made by fracturing in liquid nitrogen. They found a linear correlation between the leached matrix thickness and the volume fraction of pigment. Examination of complimentary fracture faces was required to see if leached pigment or fracture was responsible for voids. They also showed that the insoluble matrix of microtome-sectioned films was distorted.

Paint Film Weatherability

SEM examination of weathered paint films showed that chalking onsets when binder wears away from between pigment particles [*32,33*]. However, the conclusion was that SEM images point to the cause of chalking, but gloss measurements are a more quantitative and economical method.

Latex Coalescence and Adhesion

Contact diameters of various sizes of latex have been measured with SEM [*34*] and TEM [*35*] and compared to theoretical predictions. Demejo et al. [*36*] imaged with high-resolution SEM extents of latex deformation resulting from particle-substrate adhesion and compared their results to theoretical predictions.

Acknowledgments

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Infrared Spectroscopy

by Jack H. Hartshorn[1]

INFRARED (IR) SPECTROSCOPY IS AMONG THE OLDEST and most valuable of the instrumental techniques available to the coatings laboratory. It permits investigation of materials in nearly any physical form; liquid, solvent solution, cast film, ground powder, and even dried paint are amenable to this technique. While transmission of the IR beam through a thin film is the preferred mode of analysis, a wide range of accessories permit examination of nearly any kind of sample. IR provides qualitative data not easily generated by other analytical techniques. This is especially useful for probing industrial problems, where one spectrum can frequently produce all information necessary for the solution. Coupling IR instruments to computers has vastly increased their effectiveness. Spectral subtraction can often reveal hidden components and produce separations that are not practical chemically. The identification of unknown materials is now readily performed by spectral searching using digital pattern matching. The evaluation of curing, weathering, and durability chemistry can be conducted on new formulations. IR spectroscopy is currently being used to do quality assurance. Over the past four decades IR instrumentation has grown until it is now an essential part of any coatings laboratory.

INFRARED ABSORPTION

All matter either emits or absorbs radiant energy in response to its atomic and molecular structure. The electromagnetic spectrum, Fig. 1, represents that relationship. The most familiar region of the spectrum is the visible portion because that is the part we see and the paint formulator utilizes to produce his aesthetics. Immediately adjacent is the longer wavelength infrared region. This is of particular interest to the coatings analyst since organic chemicals have unique absorption bands in this range. These products include solvents, resins, polymers, additives, and a host of paint constituents. Many inorganic materials used as pigments absorb here as well. The region from 2.5 to 25 μm (or 4000 to 400 cm^{-1}) is particularly informative since here the structural bonds in organic molecules have fundamental vibrational modes. Thus, molecular compositions can be deduced from IR spectral band assignments. Structural interactions produce spectral signatures or "IR fingerprints" that can be used to identify those materials. Examination of the IR spectrum thus produces important information as to the composition of a paint film and the chemistry of a coating.

An in-depth discussion of IR spectroscopy theory and practice is beyond the scope of this chapter. However, there are a number of excellent texts on vibrational spectroscopy and IR band assignments for those interested in pursuing the subject [*1–3*]. The most useful discussion for the paint chemist is the recently updated and expanded *An Infrared Atlas for the Coatings Industry* published by the Federation of Societies for Coating Technology [*4*].

DISPERSIVE INSTRUMENTATION

Infrared spectroscopy became a practical contributor to the coatings laboratory with the development of double beam instrumentation shortly after World War II [*5*]. This instrumental design directs an IR beam through the sample and compares it with a corresponding reference beam. The spectrum is incrementally scanned to produce a graphic output of the sample's transmission characteristics. Figure 2 shows a simplified double beam IR spectrophotometer depicting the essential elements. An electrically heated wire or ceramic rod source irradiates an IR continuum. Two spherical mirrors, M_1 and M_2, focus that energy to form two equivalent rays, one for the sample and the other a reference beam. Mirrors M_3 and M_4 recombine the two at the "chopper," which alternately views each beam. The chopped beam is then routed through the monochromator, which examines each wavelength sequentially. S_1 is the entrance slit, and S_2 is the exit slit. Their function is to provide spectral resolution and to compensate for variations in source intensity and detector response. Originally, the dispersive element was a rock salt prism, but this was superseded by more energy-efficient gratings. Two or more gratings are usually required to cover the entire IR range. The detector alternately "sees" and compares the sample and reference beams. When an absorption band is detected in the sample, the reference beam is attenuated by interposing an optical wedge to match the sample's transmission. Some recent instruments have employed electronic compensation rather than mechanical blockage. The attenuator is linked to the vertical displacement of the chart pen, while the monochromator is coupled with the horizontal chart drive to produce a transmission versus wavelength or frequency presentation. An in-depth discussion of this instrumentation is available in IR texts [*4,6*] and in manufacturers' literature.

[1]Retired from Du Pont Automobile Products, Marshall Laboratory, Philadelphia, PA 19146; current address: Hartshorn Associates, Inc., Paoli Technology Enterprise Center, 19 East Central Avenue, Paoli, PA 19301.

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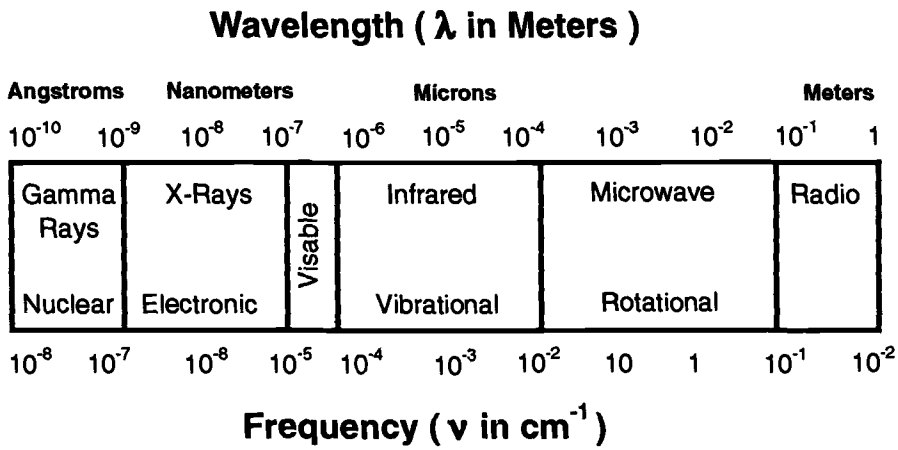

FIG. 1–Electromagnetic spectrum.

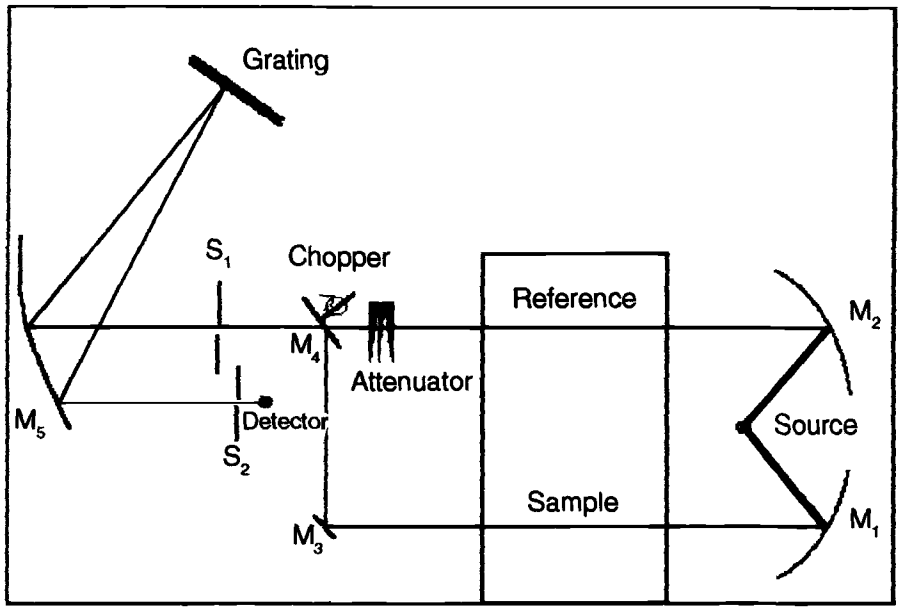

FIG. 2–Simplified double beam spectrophotometer.

Dispersive instruments have contributed substantially to our understanding of coatings and to the solution of many industry problems. However, those instruments have serious limitations that restrict many applications. Throughput energy is often inadequate for unfavorable samples and for many sampling accessories. The paper chart output requires an experienced technician for interpretation so that the value of any spectrum depends upon the skill and competency of the operator.

EMERGENCE OF FTIR

A new approach to producing infrared spectra became commercially available in the 1970s. Interferometry, or Fourier transform infrared (FTIR) spectroscopy as it is more popularly known, acquires data based upon an entirely different principle. Figure 3 shows the essential elements of a FTIR interferometer. Mirror M_1 collimates the energy from an IR source onto a beamsplitter, where the energy is divided between a stationary mirror, M_2, and a moving mirror, M_3. The two reflections are combined at the beamsplitter to produce a harmonically modulated beam. The mirror motion is precisely driven by a linear motor, and its location accurately tracked by a helium-neon laser. Its optical path (M_6 and laser detector, D_L) retraces the beam to produce that information. The interferometer's output goes through the sample compartment and is focused onto the IR detector by M_4 and M_5. Figure 4 shows a typical interferogram. A digital computer mathematically transforms the interferogram via the Fourier relationship into a traditional IR spectrum. The sample spectrum is then ratioed against a reference spectrum, which is usually taken immediately prior to the sample scan and stored in the computer. That results in the familiar transmission versus wavelength or frequency presentation. This equipment is much faster and more sensitive than dispersive instruments, and it also produces spectra with much greater precision and reproducibility. While the optics are fairly sim-

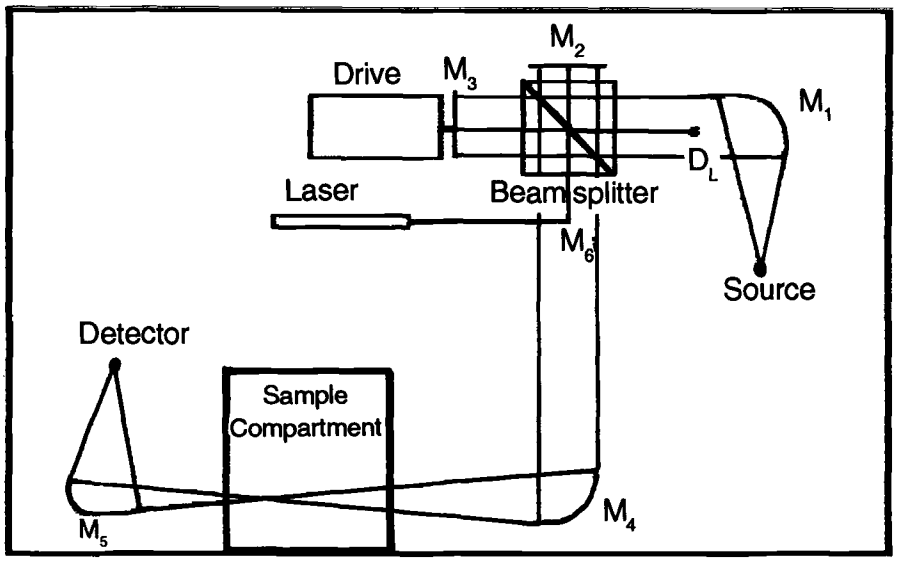

FIG. 3–Fourier transform interferometer.

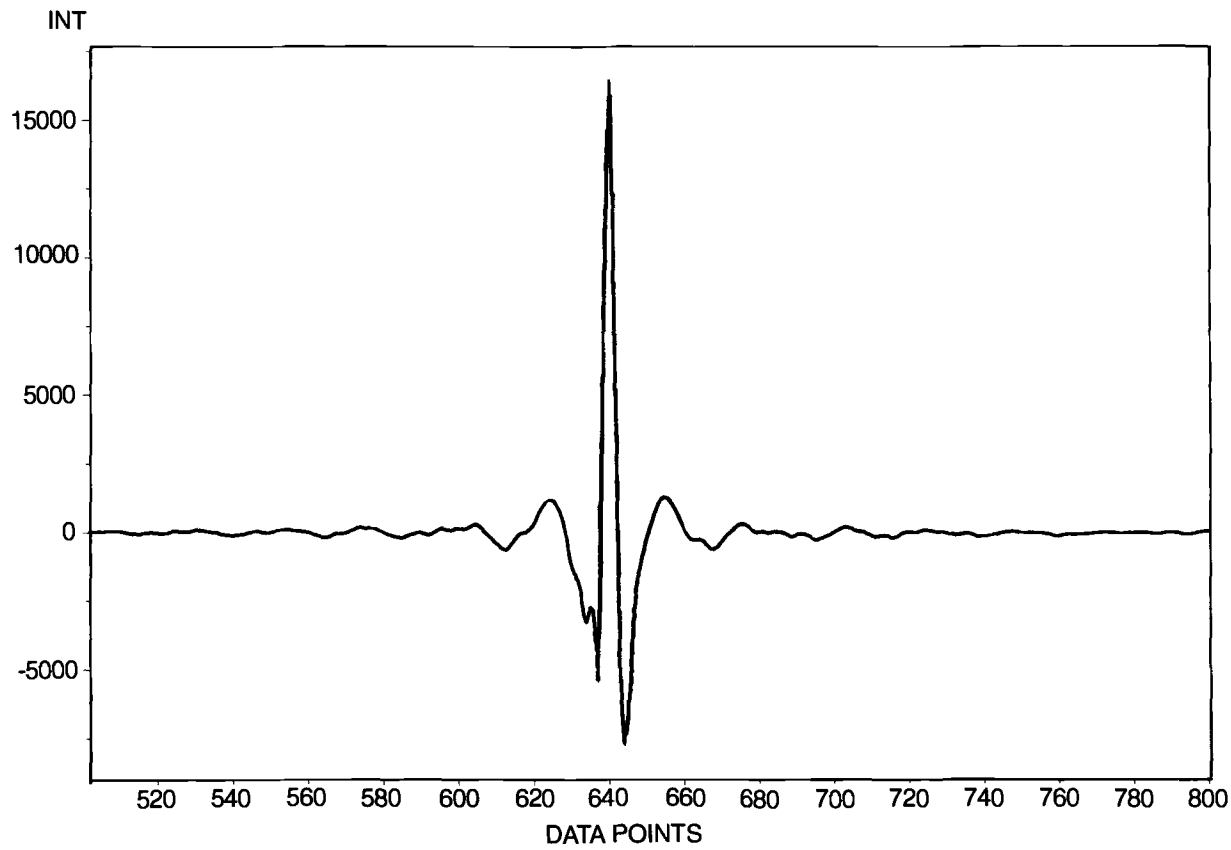

FIG. 4–Typical interferogram.

ple, the theory and calculations are complex. They have been well documented along with the advantages of FTIR [7]. These features make it extremely valuable to the coatings spectroscopist, and the enhanced capabilities permit the use of accessories and techniques that were too inefficient to be used in older instruments. The dedicated computer can also be used to produce uniquely valuable information.

SAMPLE PREPARATION

IR became popular in the paint laboratory because of the useful information that can be obtained by merely spreading the binder on a salt plate, evaporating the solvent, and scanning it [8]. This is still the method of choice whenever possible. However, not all samples can be examined as cast films,

so additional techniques have evolved to fulfill much broader requirements. Gases, which have very sharp, well-resolved spectra, need only be confined in a cell with appropriate windows to be analyzed. Gas cells are available with path lengths from a few centimeters to tens of meters. The volume is matched to the concentration of the gases to be measured. Liquids can be studied merely by squeezing them between two salt plates to produce a capillary film. These films make excellent spectra, and the intensity can be varied by changing the compression. Cells of known path length can be formed by introducing spacers of controlled thickness between the plates. Solids such as pigments are often ground with potassium bromide (KBr) powder and pressed under vacuum to produce clear pellets. Alternatively, solids can be ground in mineral oil or fluorolube and examined as mulls smeared onto salt plates. These techniques continue to be the sample preparations of choice because they are the simplest, most convenient, and have the best reproducibility. The quantity and value of the data generated are unfortunately highly dependent on the skill and experience of the operator. The best applications of this technique rely on the spectroscopist's faculty for pattern recognition and a good spectral library such as the more than 2500 spectra collected by the Infrared Spectroscopy Atlas Working Committee of the Federation of Societies for Coatings Technology [*4*].

SAMPLING ACCESSORIES

The preferred sampling method is to spread a material on a salt plate, flash the solvent, and run a transmission spectrum [*8*]. When this is not feasible, the procedures previously described are the first choices. However, our ability to examine coatings has been enhanced by a host of accessories. Their utility is greatly enhanced by FTIR's speed and sensitivity. The most successful of these techniques is attenuated total reflectance (ATR). Here, the sample is pressed against a special crystal which carries the IR beam. The optical interaction between the two appears similar to a transmission spectrum. There are, however, some major differences in band shape and intensity, which are dependant on the wavelength. ATR units are available in many configurations so that liquids, powders, films, dry panels, and almost any physical form can be accommodated.

With the advent of FTIR, a wide variety of new techniques have been developed for dealing with difficult samples and unique applications. Thin films on reflective surfaces may be investigated via specular reflectance, and rough surfaces or powders are examined by diffuse reflectance. Solids that can be heated may even be studied using their emission spectra. Dry solids and films have been investigated by detecting the sounds they produce when exposed to the FTIR beam (photo acoustic detection). Recently, infrared microscopes have become available which can focus on areas as small as 10 μm. Any of these approaches can be of great benefit to the coatings analyst, but it should be recognized that each has its own unique advantages and limitations.

DATA PROCESSING

The digital computer, which performs the Fourier transform to convert the interferogram into a normal spectrum, can also be utilized for additional tasks important to the coatings analyst. Some of these were previously thought impossible. Since the transformed spectrum is already in digital form, a variety of data processing operations, such as baseline correction, scale expansion, plot modification, smoothing, etc., can be readily performed. The computer can also execute a number of mathematical operations such as conversion to absorbance, band deconvolution, peak height measurement, and area quantitation. However, the most valuable asset is its ability to subtract one spectrum from another. This feature can be used to make separations that would be very difficult to perform chemically. The spectra are stored on magnetic disks for examination at any time and can be retrieved later without any loss in precision or integrity. Thus, samples for comparison need not be run at the same time. The computer can also rapidly compare one spectrum with a whole library of reference spectra and display the most likely choices. This can be a great blessing to the fledgling spectroscopist trying to gain experience. Finally, the computer can be preprogrammed to carry out nearly all the instrumental operations automatically. This allows the operator to concentrate on sample preparation and spectral interpretation. It also permits essentially "black box" operations by technicians.

APPLICATIONS TO ROUTINE PAINT PROBLEMS

Every paint laboratory is confronted at times by crises. The analytical laboratory is usually called upon to contribute to its resolution by answering questions like "What is this stuff?," "Where did it come from?," "What's the matter with this batch?," and "Why is this different from what we expected?." Such questions orginate from all parts of the organization—formulators and polymer chemists, plant support personnel, and customer service representatives. All these requests are important and require immediate attention. Infrared is usually the first step in executing an analysis program since it provides the most qualitative information in the shortest amount of time with the least sample preparation. Fourier transform spectroscopy makes this process considerably easier because it allows the spectroscopist to obtain a useful spectrum from almost any material. A spectrum can be obtained from nearly any amount of material that can be visually detected and isolated. If the amount is too small to see with the unaided eye, one is never certain that it is within the IR beam. With the development of IR microscopes, even this constraint is minimized. Once a spectrum is acquired, much can be learned about the material and an analysis scheme can be formulated to identify it, to isolate it, to determine its properties, and to trace the problem to its source.

For example, a common problem results when a component separates while standing in the shipping container. Figure 5 shows the spectrum of such a "float" found on the surface of a paint can. Using a micropipette, the material was drawn off and spread onto a KBr plate. Even though there

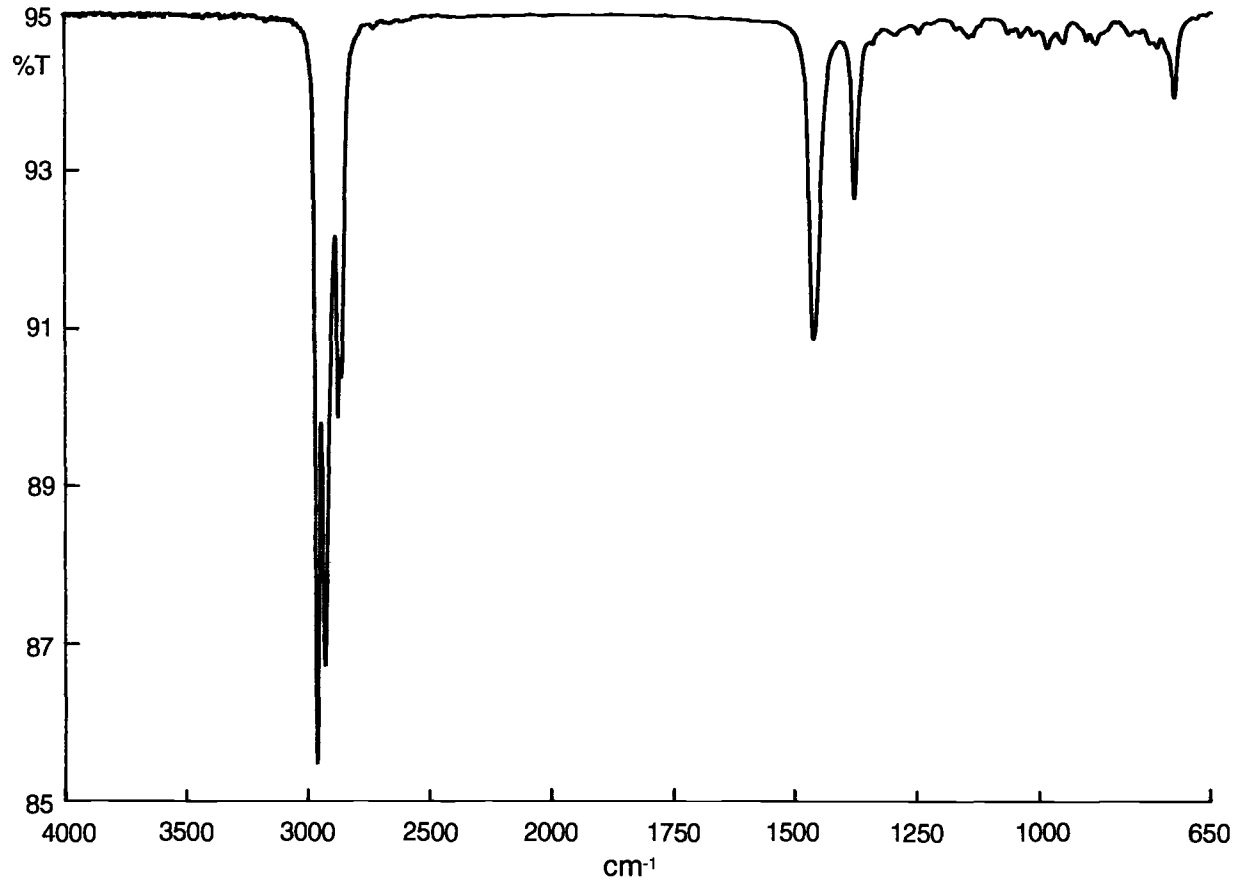

FIG. 5–Material "floating" in paint can.

was only a tiny amount of material, it was sufficient to produce a spectrum with about 10% absorption. Using scale expansion, it was identified as mineral oil. This clue led to the discovery that a shipment of cans had not been adequately degreased.

Another common problem is the "scum" that develops on the surface of panels during exposure testing. It may be caused by an exudate from within the film or it might be deposited from the environment. The amount of material is very small and is easily lost. The material can be transferred, examined, and identified by simply rinsing the exudate from the panel with a solvent and evaporating the rinse solution onto a salt plate. Figure 6 shows the spectrum of such an exudate. The infrared spectrum is that of a polyester that was not supposed to be in that formula and represented a contaminant.

DIFFERENCE SPECTROSCOPY

Probably the most useful contribution of Fourier transform spectroscopy, as far as the coatings analyst is concerned, is its ability to remove known or unwanted components so that hidden or masked materials are exposed [9]. Spectral subtraction allows the analyst to perform separations that would be difficult and time consuming or even impossible by chemical means. Interactive subtraction programs now permit the spectroscopist to manipulate subtraction factors while observing their effects on a video display. Bands resulting from known constituents can be eliminated before your eyes. One can literally strip away portions of a complex mixture to reveal the components of interest. These could be minor additives, contaminants, or possibly subtle chemical variations, but they are nearly always the components of greatest interest.

A typical resin problem illustrates this subtraction approach. Occasionally, a resin batch will not perform as expected. The assumption is always that it is contaminated and, if so, what is the contaminant? Figure 7 is the spectrum of such a contaminated acrylic resin. When compared with a good lot of the resin, it is apparent that there is a spurious band at 700 cm^{-1} and a doublet near 1600 cm^{-1}. However, the source of these bands is unknown, and it would be very difficult to isolate that component (since there is no clue as to where it originated). If the spectrum of a known "good" resin (7*B*) is subtracted from that of the "bad" one (7*A*), the contaminant's "fingerprint" is revealed (7*C*). The isolated pattern can be recognized as a phthalate plasticizer and matches the butyl benzyl phthalate reference. Total time required for this analysis is only a few minutes, far shorter than that needed for chemical separations.

In the hands of a skilled spectroscopist, subtraction is both a qualitative and quantitative tool. If the sample and reference films are carefully prepared and well matched for spectral intensity, several components can be sequentially stripped from the spectrum to reveal very minor constituents.

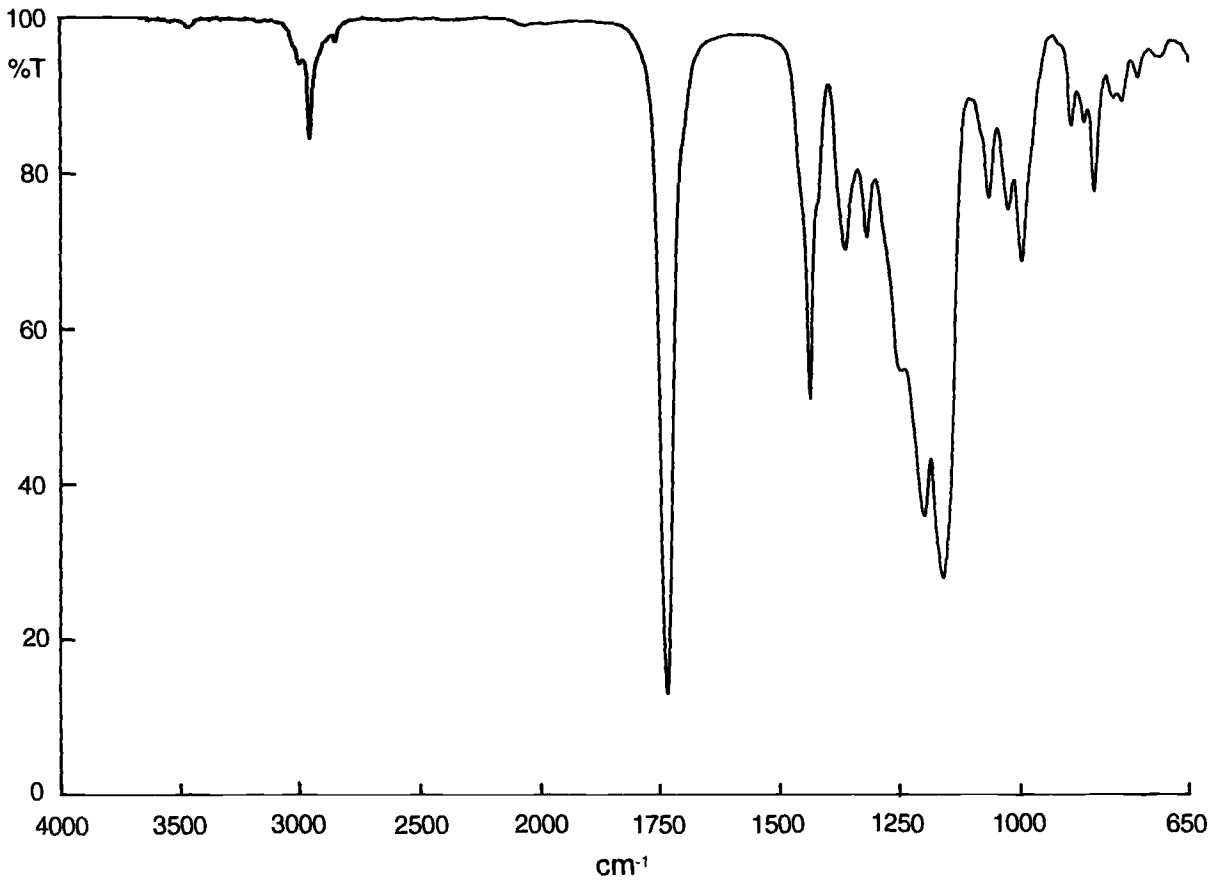

FIG. 6–"Scum" from exposure panel.

This must be done very carefully with considerable knowledge of the system, otherwise a noninterpretable jumble of both positive and negative peaks will result. Alternatively, one may spectrally add the individual components together mathematically and then perform the subtraction. The safest method of difference spectroscopy is a comparison between the unknown and a known composition where the reference is a model synthesized from recognized chemical ingredients. With care, the subtraction factors can be used to estimate the concentration of each component. This may be sufficiently accurate for many applications. With a range of calibration samples, multicomponent analysis can be employed to determine the various constituents. Usually it is prudent at this point to shift to another analytical technique if a more quantitative result is required.

SPECTRAL SEARCHING

Fourier transform instruments are usually offered with spectral searching algorithms as a part of their software package, either included with the equipment or as an additional option. Several third party search packages are also available. These can be very helpful to the coatings spectroscopist, particularly the novice. They provide a quick way to eliminate the majority of possibilities so that one can concentrate on the best fits in their quest to discover what an unknown spectrum is chemically. Several approaches, such as peak matching and vector analysis, have been employed; however, the objective is the same—they all endeavor to pick the best matches to an unknown spectrum from a spectral reference library database [*10*]. These libraries may be generated internally or they can be purchased as a commercial collection, such as those developed by the Federation of Societies for Coatings Technology, Aldrich Chemical Co., and Dieter Hummel. All are available from Nicolet Instrument Corp. One deficiency in this approach is that no search system can find a match for a spectrum not included in the library. However, closely allied matches can suggest possibilities that are helpful in identifying an unknown. One must always compare the actual spectrum with the library reference since even high scoring matches can be wrong and may be misleading. Most laboratories eventually choose to produce their own libraries because it makes searching much faster and the "hits" more accurate.

Another plant-type crisis shows how ingenuity, subtraction, and searching can be used to solve a difficult problem. Sometimes a batch of liquid resin is not as clear as expected. This is often referred to as "cloud" or "haze." The "cloud" can often be concentrated by centrifuging the resin. The contaminant will either be forced to the top or sink to the bottom of the tube. Figure 8 is the spectrum of a hazy resin which was centrifuged. The concentrated material from the bottom of the tube was then spread onto a KBr plate for examination (8*A*). Most of the spectrum is the resin, and only a hint of the "cloud" can be detected. By subtracting the spectrum of the

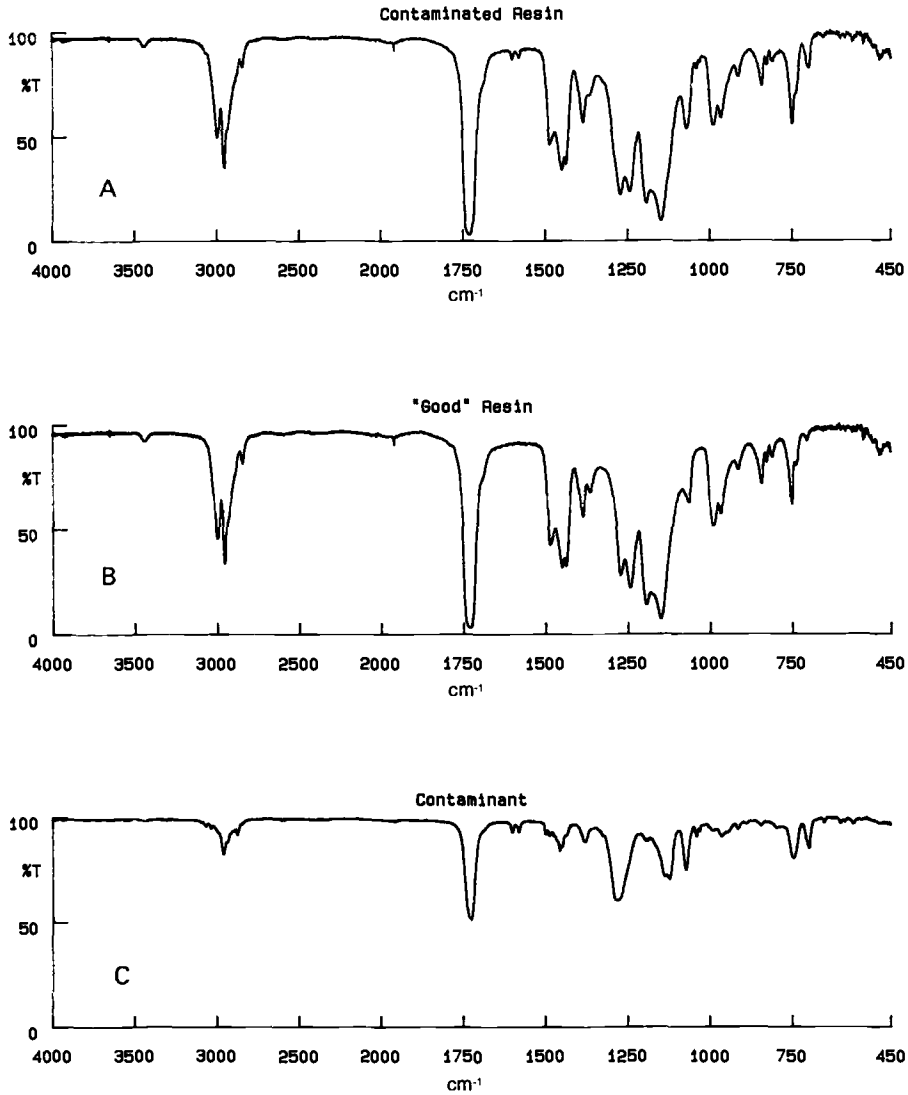

FIG. 7–Resin contaminant isolation.

centrificate (8*B*), the pure spectrum of the haze can be isolated (8*C*). A search of several libraries indicated the best match would be a silica. Silica flock is very often used as a filter aid. Apparently a small hole had developed in one of the process filters, allowing the filter aid to leak through and contaminate the batch.

TIME LAPSE SPECTROSCOPY

Digitized Fourier transform spectra are readily stored on magnetic disks media and can be retrieved at some later time without any lose of accuracy or integrity. This allows spectra to be accumulated over a period of time and compared at leisure. Thus, cure studies may be carried out over hours, days, or weeks, while durability and weathering tests may extend to years. By repeatedly examining the same point within a film, very subtle chemical changes can be detected. This technique is used to determine cross-linking reactions taking place during cure and the degradation resulting from exposure to the elements, i.e., weathering. If spectra are taken and stored at frequent, regular intervals, the course of these reactions can be followed. The spectra may then be likened to the single frames of "time lapse" photography [*11*]. Since the spectral bands are a result of the chemical composition within a film, the chemical changes taking place can be assessed by carefully examining the spectral shifts occurring during that time. In this manner, not only overall conversions, but sequential reactions can be detected. If the intensity of the disappearing bands is measured and correlated with time, reaction rates can be determined [*12*].

QUALITY ASSURANCE

Fourier transform spectroscopy's greatest contributions to the coatings industry have just begun. The recent increased emphasis on product quality makes automated analytical techniques not only practical but necessary to remain competitive. Using computerized spectral subtraction, a fraction of a percent of a foreign material can be detected and identi-

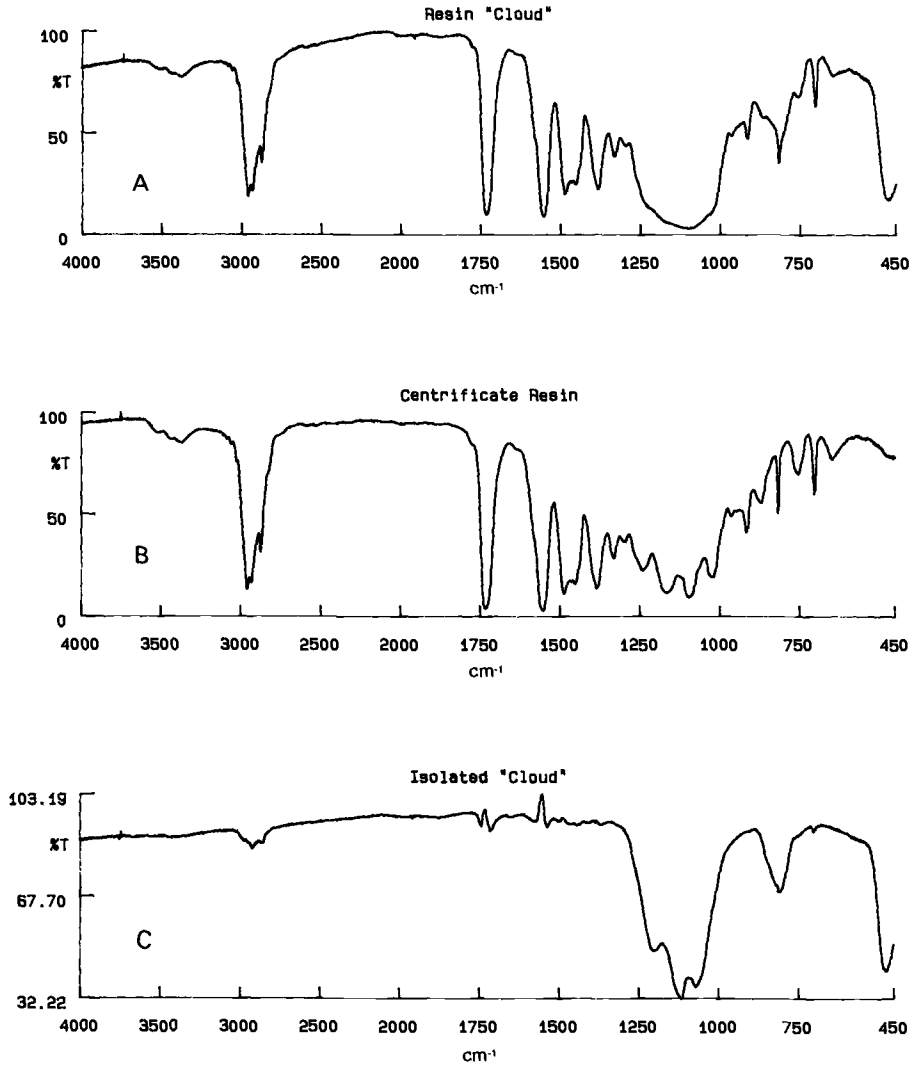

FIG. 8–Resin "cloud" identification.

fied. By preprogramming the spectrometer computer, the spectroscopic functions can be relegated to the background so that it becomes, in effect, a "black box." An operator with minimum training can perform very sophisticated analyses by simply pressing a few buttons. By applying these principles, a system for testing incoming raw materials, manufactured intermediates, and finished products has been developed [*13*]. These programs allow a control laboratory operator to call up a stored standard spectrum, run the current sample, make a comparison, and determine a "goodness of fit" factor—all automatically—in less than 5 min.

CONCLUSIONS

Infrared spectroscopy has proven over the years to be one of the most valuable problem-solving tools available to the coatings analyst. It is usually the first technique applied to difficult analytical problems because it provides unique information about samples in almost any physical state. The extent of the problem can then be assessed and a plan of attack formulated. The advent of FTIR has removed most restrictions imposed by sample size and form. A wide variety of attachments is available that greatly expands the range of samples amenable to examination. Its associated computer allows the analyst to strip away known components to reveal minor additives and contaminants. Spectral subtraction can thus perform separations which would be difficult if not impossible by other means. Data-handling techniques are proving to be the most valuable contributions of this technology for the paint industry. Spectral identification of unknown materials via computer pattern matching has become common place. Digital spectral storage and retrieval permits comparison of films as a function of time so that the chemistry taking place during cure and exposure can be followed. It can also determine when and at what rate those reactions are taking place. The ability to preprogram the spectrometer allows relatively unskilled operators to perform very sophisticated analyses without being burdened by spectroscopic functions. The instrument can then become an automated "black box" quality assurance analyzer.

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Methods for Polymer Molecular Weight Measurement

74

by Thomas M. Schmitt[1]

THE BINDERS USED IN COMMERCIAL COATINGS are organic polymers, the molecular weights of which greatly influence the properties of the final coating [*1*]. As a necessary result of the manufacturing processes, synthetic polymers are mixtures of compounds of similar molecular structure but varying molecular weight. For an exact understanding of the system, one must know the molecular weight and weight (or mole) fraction of each species, in other words, the molecular weight distribution. For many practical purposes, an average value of molecular weight suffices. The final cured paint film is generally a cross-linked system resembling a single massive molecule, where the concept of molecular weight has little meaning. Molecular weight determination is thus applied only to coating formulation ingredients.

Many procedures have been used to determine molecular weight. We will limit our discussion to the most practical methods, for which commercial instrumentation is available at reasonable price. Both archaic and research methods will be omitted, as will those methods which are only suitable for determination of low molecular weight compounds.

MOLECULAR WEIGHT DEFINITIONS

While the molecular weight of a single molecule is a simple concept, there are several ways to calculate the molecular weight of a mixture. The most useful values are number average molecular weight, $\overline{M_n}$ and weight average molecular weight, $\overline{M_w}$

$$\overline{M_n} = \frac{\sum_i n_i M_i}{\sum_i n_i} \qquad \overline{M_w} = \frac{\sum_i w_i M_i}{\sum_i w_i}$$

where M_i denotes the molecular weight of component i, n_i is the number of moles of component i, and w_i symbolizes the total weight of component i and is thus equal to $n_i M_i$. Weight average molecular weight is necessarily equal to or higher than number average molecular weight. A mixture of equal numbers of two molecules, one weighing 100 and the other weighing 1000, has a $\overline{M_n}$ of 550 and a $\overline{M_w}$ of 918. The polydispersity of this mixture, $\overline{M_w}/\overline{M_n}$, is 1.7. This indicates that most of the mass of the example mixture consists of higher molecular weight material, but that comparatively small molecules are also present. The higher the value of $\overline{M_w}/\overline{M_n}$, the broader is the distribution of weights of molecules in the sample. Two other measures of molecular weight have found acceptance because they can be directly measured by certain techniques: z-average molecular weight, $\overline{M_z}$, and viscosity average molecular weight, $\overline{M_v}$

$$\overline{M_z} = \frac{\sum_i w_i M_i^2}{\sum_i w_i M_i} \qquad \overline{M_v} = \left[\frac{\sum_i w_i M_i^a}{\sum_i w_i M_i}\right]^{1/a}$$

For the above-mentioned mixture of molecules of weight 100 and 1000, the z-average molecular weight is 991. Clearly, if the actual distribution of M_n, M_w, or M_z is known, the distributions and average values of the other two parameters may be calculated. The exponent a is obtained from the Mark-Houwink equation and is specific to polymer type and branching as well as the temperature and solvent of the measurement system [*2*].

Which molecular weight value is of greatest significance, number average, weight average, z-average, or viscosity average depends upon the particular application of the polymer mixture. Knowledge of M_n and M_w is sufficient for most purposes. M_n is often critical to stoichiometry of curing reactions and controls some properties. For coatings, many of the properties of the final product are controlled by M_w, with M_w/M_n also playing an important part.

METHODS FOR DETERMINATION OF NUMBER AVERAGE MOLECULAR WEIGHT

End Group Analysis

Some polymers used in coatings have reactive end groups which participate in the curing reactions. Assuming that the degree of branching is known and that the end of each polymer chain has such a group, methods for routine quality control may be based on determination of end groups. Since each molecule has the same number of end groups, the result is a number-average molecular weight. Polyurethane raw materials fit this description, and "wet chemical" methods are well-established for rapid and accurate analysis of these compounds. Hydroxy-terminated compounds are analyzed by determination of hydroxyl number [ASTM Method for Testing Polyurethane Polyol Raw Materials: Determination of Hydroxyl Numbers of Polyols (D 4274)]. Isocyanate-terminated prepolymers are analyzed by ASTM Test Method for Polyurethane Raw Materials: Determination of Amine Equivalent of Crude or Modified Isocyanates (D 4666). End group analysis

[1]Manager, Research Services, BASF Corp., 1419 Biddle Avenue, Wyandotte, MI 48192-3736.

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is not limited to polyurethane raw materials. Amine or carboxylic acid functional groups may be determined by acid-base titration, often in non-aqueous solvents, but the parameters of solvent, titrant, and apparent pH at the end point must be worked out for each compound.

End groups may also be determined by spectroscopic methods, usually infrared and nuclear magnetic resonance spectrometry. For example, see ASTM Method for Testing Polyurethane Raw Materials: Determination of Primary Hydroxyl Contents of Polyether Polyols (D 4273).

Even polymers which are not usually thought of as possessing functional end groups may be analyzed. This is because molecules are often terminated by fragments of the catalyst which initiated the reaction. An example is polyacrylonitrile, which may be terminated by a sulfate or sulfonate group. The analyst familiar with the mechanism of polymerization (which should not involve a high percentage of chain terminations which do not leave the desired end group) can often devise a way to measure the molecular weight based on determination of these residues.

Accurate measurement of $\overline{M_n}$, by end group analysis is limited to polymers of molecular weight less than about 20 000, since the end group concentration is too low for precise measurement above this range.

Colligative Properties Analyses

$\overline{M_n}$ may be determined based on colligative properties, i.e., based on measuring changes in solvent properties which are due to the number of molecules dissolved. These properties include vapor pressure, freezing point, boiling point, and osmotic pressure. By derivation from fundamental equations [*2–5*], it can be shown that, at low concentration, the relationship between a colligative property and molecular weight reduces to

$$\overline{M_n} = \frac{KC}{\Delta X}$$

where K is a constant specific for the solvent, C is the weight/volume concentration of the polymer, and ΔX represents the observed change in the colligative property.

K is best determined experimentally, rather than calculated. For the best accuracy, several measurements are made so that the value of $\frac{\Delta T}{C}$ can be extrapolated to find the limit at zero concentration. These techniques are more often used in research laboratories than for quality control purposes. Boiling point elevation and freezing point depression are rarely used for polymers since instrumentation suitable for observation of small temperature differences is not commercially available.

Small molecules have a disproportionate effect on the number average molecular weight. For example, the presence of 0.1 wt% water contaminating a 20 000 $\overline{M_n}$ polymer will result in return of a colligative property value of 9500 for $\overline{M_n}$. This effect is amplified as polymer $\overline{M_n}$ increases. Thus, moisture and solvent must be completely removed prior to analysis. Commercial polymers are first purified by extraction or by dissolution and precipitation to remove additives such as stabilizers and lubricants.

For determination of molecular weight by **membrane osmometry,** a solution of the test substance is separated from pure solvent by a semi-permeable membrane, i.e., a membrane which is permeable to low molecular weight solvent molecules but impermeable to molecules of the test substance. Because of the lowered activity of solvent containing the polymer, solvent molecules will tend to travel across the membrane from the pure solvent. The pressure which must be applied to the solution to equalize this flow is equivalent to the osmotic pressure. Because the change in osmotic pressure is dramatic compared to the small temperature changes observed with the other colligative property methods, membrane osmometry is useful for higher molecular weights, up to about $\overline{M_n} = 10^6$, although accuracy fades at the highest values. The technique cannot be used for low molecular weights because commercial membranes are not sufficiently selective: typically, manufacturers quote cutoff values of 5000 to 20 000 for various membranes, indicating that molecules below that value can permeate the membrane. This property can actually be an advantage in that it is not necessary to purify the polymer to remove low molecular weight additives: their concentration is quickly equalized on each side of the membrane, so that their presence does not affect the molecular weight value. Elevated temperatures may be used with less soluble polymers, but choice of membranes becomes limited as the temperature is increased and as less common solvents are selected.

Vapor pressure osmometry actually is unrelated to osmometry, consisting simply of the measurement of vapor pressure depression in order to determine molecular weight. Commercial instruments measure the vapor pressure indirectly: the vapor pressure difference between a dilute polymer solution and pure solvent is measured by monitoring the temperature difference between drops of each liquid in equilibrium with solvent vapor. Although in principle this is an absolute measurement, in practice these instruments are calibrated with standards of known $\overline{M_n}$. Vapor pressure osmometry complements membrane osmometry in that it is suitable for materials with $\overline{M_n}$ in the range below 20 000, with accuracy dropping off at higher molecular weights because of the very small temperature differences observed.

The experimental procedure is described in ASTM standard D 2503 (Test Method for Molecular Weight of Hydrocarbons by Thermoelectric Measurement of Vapor Pressure), although the manufacturer's literature for the specific apparatus must be considered definitive.

DETERMINATION OF WEIGHT AVERAGE MOLECULAR WEIGHT BY LIGHT SCATTERING

Unlike $\overline{M_n}$, $\overline{M_w}$ is not much affected by the presence of small quantities of low molecular weight impurities. The only common method for direct determination of $\overline{M_w}$ is light scattering. Light is scattered by polymer solutions in a manner which is well understood theoretically and which depends upon the size of the polymer molecules in solution. Classical measurement of $\overline{M_w}$ by light scattering is described in an ASTM standard [Practice for Determination of Weight-Average Molecular Weight of Polymers by Light Scattering (D

4001)]. The technique is usually performed by specialists because of the attention to detail required for accurate values: (1) Traces of dust and other particles must be removed from the solutions; (2) Light scattering measurements formerly needed to be made manually at several angles.

Modern laser light sources make possible measurement of light scattered at angles less than 10° [2]. At such low angles, the equations defining the relation of M_w to scattered light are reduced such that measurement at a single fixed angle is sufficient. Simple measurement of a set of dilute solutions of the polymer to determine scattered light and the concentration dependance of the solution refractive index (RI) suffice to determine $\overline{M_w}$. Instruments are also available which make measurements at multiple angles automatically, so that the radius of gyration as well as the molecular weight of the substance may be determined. With either the low-angle or multiple-angle instruments, operation is no more tedious than if a single measurement were made on each solution. An advantage of the laser light sources is that their intensity makes the sample size requirement lower, so that much less solution need be filtered free of particulates. If the instrument is designed so that the sample solution flows through the cell, interference from particulates is apparent as random sharp spikes, which may be corrected electronically before performing molecular weight calculations.

Light scattering is less suitable for analysis of polymers of $\overline{M_w}$ lower than about 20 000. However, the low-range sensitivity increases as the RI difference between solvent and polymer increases. Methods for molecular weight determination for light scattering are well described in the literature [2–5], but the instructions of the instrument manufacturer are most relevant.

SIZE EXCLUSION CHROMATOGRAPHY

Size exclusion chromatography (SEC) is a type of high performance liquid chromatography (HPLC) in which separation is made on the basis of the size of the molecules in solution [6–7]. It is often called **gel permeation chromatography** (GPC) since the separating medium was historically a swollen polymer gel. The stationary phase is now most often a rigid packing containing pores of the same order as the size of the molecules in the sample. As a sample of a disperse polymer is pumped through the HPLC column, smaller molecules penetrate further into the stationary phase than do larger molecules, with the result that the smaller molecules elute after the larger.

SEC determines size in solution versus standards. Because the interaction of a polymer with a solvent changes as a function of molecular weight, size in solution does not necessarily have the same relationship to molecular weight over a large molecular weight range. Thus, SEC is not an absolute method for determining either $\overline{M_n}$ or $\overline{M_w}$. In spite of this, it is today unquestionably the most widely used procedure for determination of both. SEC has the very great advantage that the polymer need not be purified of additives, oligomers, and residual monomers before analysis. Indeed, SEC can sometimes be used for the determination of these components simultaneously with the characterization of the polymer itself.

SEC Instrumentation

SEC instrumentation consists of a basic HPLC system, including a constant volume pump, injector, column set, detector, and computerized data handling system. HPLC is discussed in another chapter. The *pump* must be capable of delivering solvent with greater precision than is necessary for ordinary HPLC, preferably within 0.1%. This is because of the semilogarithmic SEC calibration curve, where small differences in elution volume result in a large difference in apparent molecular weight. Alternatively, some device may be used to continuously monitor flow rate so that experimental data may be replotted in terms of elution volume rather than elution time. Another approach is use of an "internal standard," usually of very low molecular weight, to permit correction of experimental retention times. Such devices are rarely used nowadays, since the variations they introduce are of the same magnitude as the variations in flow of modern, well-maintained HPLC pumps. Control of the *temperature* of the system is desirable since fluctuations in ambient laboratory temperature add variation to retention times and, more seriously, cause drift in the baseline of the refractive index detector. Ideally, the entire unit is encased in a constant temperature chamber. Unfortunately, these enclosures usually must be constructed by the user because of the limitations of commercial units. Many users make do with temperature control of only the column chamber and the detector, which suffices if the laboratory temperature remains somewhat constant.

SEC *columns* are usually filled with styrene/divinylbenzene copolymer and are always purchased pre-packed. Modern instrument manufacturers supply columns of a uniform high performance. For increased resolution, more than one SEC column is used in series, with as many as four or five 30-cm columns being preferred by many operators. These may consist of diverse columns, each containing packing of a specific pore size, or each may contain packing of broad pore size distribution.

Various *detectors* are used in SEC. The most common is based on detection of changes in refractive index (RI) of the solvent as the solute elutes. This property is closely related to concentration and such a detector is suitable for any material with an RI which differs from that of the solvent. Commercial detectors are designed to minimize temperature fluctuation since RI is strongly dependant upon temperature. Temperature control can be either active (electronic heating devices) or passive (massive metal block surrounding the cell). The mass response of the refractive index detector varies by only a few percent with molecular weight, and it is thus assumed to be a linear concentration detector. It is well to check this assumption if analyses will straddle a broad molecular weight range, particularly at the low end of the range. Caution must be used in the analysis of copolymers since the RI of copolymers changes with composition.

Other detectors are used for special purposes. A UV absorbance detector, usually in series with an RI detector, is suitable for analysis of polymers with strong chromophores, such as those containing styrene, terephthalate, or bisphenol A groups. Infrared absorbance detectors are used to track particular components of the polymer, but limitations in useful wavelengths and solvents prevent their general use. Another

detector is based on "evaporative light scattering." In this instrument the solvent is evaporated as the SEC effluent passes through a gas stream. Any non-volatile solute is converted to a fine aerosol, which is detected by its ability to scatter a light beam. Another detector, based on differences in dielectric constant between solvent and solution, has many of the advantages of the RI detector, but is not widely available. Caution must be used when applying any detector, since, if the response is not linearly proportional to concentration over a wide molecular weight range, calculation of molecular weight distribution from experimental data will result in serious errors.

Two specialized detectors are worthy of mention: A viscosity detector gives an instantaneous readout of the viscosity of the solution eluting from the chromatograph. It is used in series with an RI detector so that both concentration and viscosity of the eluent are determined, permitting estimation of intrinsic viscosity and hence molecular weight. There are low-angle and multiple-angle laser light scattering instruments designed for use as SEC detectors. Like the viscosity detectors, they are used together with a mass sensitive detector, usually an RI detector. A characteristic shared by both detectors is their intrinsically greater sensitivity as the M_w of the solute increases. Thus a trace of high polymer or undissolved material that might be undetected by refractive index appears as a major component to a light scattering detector. Whether or not this sensitivity is advantageous depends on the application. Viscosity and light-scattering detectors are commercially available, reasonably priced, and reliable. Still, they remain very much the province of the specialist. This is because the additional information which they provide is not essential for most practical applications. They are not used for routine analysis of paint components nor are they typically used by synthetic chemists.

An *autosampler* is a valuable accessory for GPC, more so than for other forms of HPLC. This is because the long analysis times typical of SEC and the rigorous calibration procedures make it difficult to attain high sample throughput unless the usual 8-h day can be extended. If the column and mobile phase are rarely changed so that calibration is required infrequently, manual injection is practical.

Calibration and Calculations

SEC is a relative technique which requires calibration with standards of known molecular weight. The calibration curve is semilogarithmic, with the SEC columns usually chosen such that retention volume is linearly proportional to the logarithm of molecular weight over a broad range. Calibration is greatly simplified if specially prepared standard materials of low polydispersity can be used.

The choice of standards is critical since the relationship of retention time to molecular weight varies with different polymers, even those in the same chemical family. Since it is the size of the solvated polymer rather than its molecular weight which determines elution volume, significantly different calibration curves are obtained from branched and linear molecules. The most easily obtainable standards are of polystyrene. Polystyrene has a higher molecular weight for the same chain length than do aliphatic polymers, so a polystyrene calibration curve will give high results for the molecular weight of many common polymers. The method of calibration should always be reported when SEC molecular weight values are given.

A **universal calibration** system has been devised based on the relationship between viscosity and SEC retention time, since each is a function of the size of the solvated polymer. When using universal calibration, standards and samples may be quite different polymers; it is only necessary that the Mark-Houwink coefficients for standards and samples be known. Of course, the Mark-Houwink coefficients must be known for the polymer in the particular SEC solvent at the temperature used. Obtaining these coefficients is not as demanding a task as preparing narrowly distributed standards of a new polymer, and universal calibration has found widespread use. The approach is sufficiently popular that it is described in an ASTM standard: ASTM Test Method for Molecular Weight Averages and Molecular Weight Distribution of Certain Polymers by Liquid Size-Exclusion Chromatography (Gel Permeation Chromatography-GPC) using Universal Calibration (D 3593).

Most analysts use computerized data systems for evaluation of SEC data. These systems are reasonably priced and aid the operator in all phases of data treatment, from preparation of the calibration to determination of molecular weight averages to preparation of attractive graphs of molecular weight distribution. Caution must be used in their application; not all systems will give the same results as an intelligent operator performing manual calculations. The greatest difficulty is in mathematical representation of the calibration curve of retention time versus molecular weight. Use of higher order equations to represent the calibration can introduce large errors compared to simply connecting the experimental data points.

SEC data for narrow molecular weight distributions must be corrected for dispersion contributed by the instrumentation. This correction is not significant for the broad molecular weight distributions typically found in coatings. Band broadening corrections become more important if a molecular weight-sensitive detector is used, such as a viscometer or light-scattering instrument.

SEC procedures and calculations are thoroughly described in ASTM Test Method for Molecular Weight Averages and Molecular Weight Distribution of Polystyrene by Liquid Exclusion Chromatography (Gel Permeation Chromatography—GPC) (D 3536).

Application of SEC

SEC may be performed with either aqueous or organic solvents. Non-aqueous systems are more reliable, but, of course, water-soluble compounds such as polyacrylates are more readily analyzed in aqueous solvents. Non-size exclusion interactions between the column and sample are more common with aqueous systems. These undesirable interactions include adsorption and ion exclusion/ion retardation and can often be controlled by adding salts or a low percentage of organic solvent.

Elevated temperature is necessary for the analysis of some polymers because of their low solubility or because of the high viscosity of the solvents which they require. In general,

this is not a consideration for the relatively low molecular weight polymers used in coatings raw materials.

SEC has long since spread from the specialized central laboratory to the laboratory of the synthetic and formulating chemist. Central analytical laboratories select the SEC column set and mobile phase for optimum resolution of a particular polymer and molecular weight range. Central laboratories also typically perform extensive calibration. Practice in synthesis laboratories is usually different, with a single system used in a comparative fashion for all analyses. Indeed, when SEC is used routinely by resin chemists to follow polymerization reactions, the fine details of calibration are typically ignored and molecular weight is estimated by simple comparison to polystyrene standards, either by visual estimation of "peak" molecular weight or by uncritical acceptance of the default computer-generated report. For most troubleshooting applications, it is enough to overlay the chromatograms of a "good" and a "bad" polymer in order to determine whether differences in molecular weight distribution contribute to a problem. In the case of a product which does not have a single smooth molecular weight distribution but rather consists of two or more discrete distributions, visual comparison of peaks is often more valuable than comparison of numerical values. To monitor a polymerization reaction, it may be enough to watch the gradual disappearance of the peaks due to monomers.

VISCOMETRY

Rheology of paint components is discussed in Chapter 33. We will discuss here only viscosity measurement to determine molecular weight.

Solution viscometry is the method of determining molecular weight most suitable for routine quality control. The viscosity/concentration relationship of a polymer solution is a function of the chain length of the polymer, so viscosity can be used as a measure of molecular weight.

As with other methods, determination of true molecular weight by solution viscosity requires purification of the polymer and extrapolation to zero concentration of a series of ratios representing measured values. The zero intercept, representing the limit of the viscosity/concentration relation as zero concentration is approached, is the intrinsic viscosity, $[\eta]$. It is related to $\overline{M_v}$ by the relationship expressed in the Mark-Houwink equation

$$[\eta] = K\overline{M_v^a}$$

The constants for the Mark-Houwink equation must be determined experimentally using well-characterized polymer standards of narrow $\overline{M_w}/\overline{M_n}$. ($\overline{M_w}/\overline{M_n}$ must be small for valid calibration since $\overline{M_v}$ is numerically different than $\overline{M_n}$ or $\overline{M_w}$.)

Since viscosity is determined by the hydrodynamic volume of the polymer, the relationship with molecular weight is specific for the polymer, the solvent, the temperature, and, of course, the concentration. A relationship determined for a linear polymer will not be accurate if branched molecules are also present. This means that the constants in the Mark-Houwink equation change with various solvents and with polymers having various degrees of branching. Measurements are made at high dilution to minimize the effect of variables other than molecular size. Capillary viscometers, used to measure the solution flow rate at a specific pressure differential, are most generally suitable. Procedures for determination of solution viscosity are contained in Test Method for Diluted Solution Viscosity of Polymers (D 2857), as well as in the other ASTM standards referenced in D 2857.

It is unfortunately not possible to discuss this subject without defining a number of viscosity relationships:

Relative viscosity is the parameter which is actually measured when viscosity is determined. It is the ratio of efflux times for the polymer solution versus pure solvent:

$$\eta_{rel} = t/t_0$$

where t and t_0 are the efflux times for polymer solution and pure solvent, respectively. **Reduced viscosity** takes concentration into account:

$$\eta_{red} = \frac{t - t_0}{t_0 C}$$

where C represents the polymer concentration, usually in grams per 100 mL. **Intrinsic viscosity** is determined by plotting against concentration several values of reduced viscosity, extrapolating to obtain the intercept at zero concentration:

$$[\eta] = \lim_{C \to 0} \eta_{red}$$

where $[\eta]$ represents intrinsic viscosity.

Some workers determine Mark-Houwink constants with unfractionated polymers of measured $\overline{M_w}$, thus relating viscosity to $\overline{M_w}$ rather than $\overline{M_v}$. This non-rigorous approach is viable because $\overline{M_v}$ is usually rather close to $\overline{M_w}$.

Solution viscosity is an excellent method for routine QC of relatively uniform polymers. A single analysis at a fixed concentration and temperature will indicate that the product falls into the stated molecular weight range. For example, ASTM Test Method for Determining Inherent Viscosity of Poly(Ethylene Terephthalate) (PET) (D 4603), describes a method for determining **inherent viscosity** (natural log of relative viscosity, divided by concentration). ASTM Test Method for Intrinsic Viscosity of Cellulose (D 1795) describes a one-point procedure for estimating intrinsic viscosity. The results of such measurements can be related to molecular weight and are useful for predicting properties of different batches of well-understood commercial resins. Many polymer chemists routinely make one-point viscosity measurements to monitor synthesis experiments, reserving more sophisticated molecular weight measurements for products chosen for commercialization.

Melt viscosity, the viscosity of the pure polymer, is correlated with $\overline{M_w}$. Equations developed to relate degree of polymerization with melt viscosity use a temperature-dependant function which differs for each polymer system. As a practical matter, polymer melts are non-ideal fluids, and their true viscosity cannot usually be measured with simple equipment. Thus, melt viscosity is usually determined because of its significance to polymer processability, rather than as an estimate of $\overline{M_w}$. **Pour point,** the temperature at which the polymer begins to flow, is similarly related to molecular weight, and may be used to estimate it.

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Coatings Characterization by Thermal Analysis

by C. Michael Neag[1]

THERMAL ANALYSIS (TA) ENCOMPASSES A VARIETY of techniques used to measure changes in material properties with changes in temperature. These techniques apply broadly in materials science and find use in characterizing liquids, polymers, and inorganic materials. The many results obtained using TA fit neatly into Van Krevlan's [*1*] classification of material properties. He divides material properties into three distinct but interrelated categories: (1) intrinsic properties, (2) processing properties, and (3) product or article properties. Intrinsic properties such as the glass transition temperature (Tg) or elastic modulus arise from the chemical and physical structure of a material, can be measured with precision, and may form the basis for predictive empirical relationships. A material's process properties depend on the interplay of intrinsic properties and process conditions (e.g., synthesis temperature or mixing time). In essence, they reflect a material's intrinsic properties in a dynamic environment. In practice, the interaction of a material's intrinsic properties and process properties yield a unique product embodying still different properties. Unfortunately, the relationship between intrinsic properties and process properties is poorly understood, difficult to measure, and more difficult to predict. Because product properties depend on this ill-defined relationship, their meaning becomes quite subjective. Simply put, a paint made and applied one day may behave quite differently than a paint made and applied another day, and the reasons for the observed differences often remain obscure.

Thermal analytical techniques provide tools to help clarify these hard-to-understand relationships, helping to reduce product development time and manufacturing costs, while shaping the best possible product. The instrumentation supporting thermal analysis has grown remarkably in both versatility and sophistication: automated systems, absolute control of applied stresses, and tenth-of-a-degree temperature resolution have replaced strip chart recorders, spring-loaded stresses, and "give or take a degree" temperature resolution.

The advent of the inexpensive microprocessor chip probably represents the most significant step in the development of improved commercial thermal analyzers. The development of powerful PC and microcomputer-based controllers have dramatically simplified experimental procedures, data collection, and data analysis in thermal analysis. In general, automating these instruments has dramatically improved the experimenter's control over the sample environment. These improvements allow technologists to complete complex experiments involving multistep heating programs and several purge gases. At the same time, calibration routines were also simplified and the accuracy and precision of the results improved. All of these advances came with the additional benefit of unattended operation. In fact, several commercial suppliers offer instruments with robotic control that permit the analysis of scores of samples at the touch of a button.

The simple yet highly sophisticated character of these instruments has a major drawback: their simplicity significantly increases the potential for misinterpreting experimental results. With advances in automation, thermal analytical techniques have moved closer to simple "turn-key" operations and have reduced considerably the technical demands on the user. TA has become a marvelously simple process that unfortunately requires little understanding of the instrumentation or the results. A few minutes in sample preparation yields a raft of data from sophisticated data analysis software, considerably increasing the potential for error in data interpretation or analysis. The improvements in instrumentation and software demand greater caution from the scientist in experimental design and results interpretation. Wendlandt [*2*] and Earnest [*3*] discuss the advent of automation in thermal analysis, and two volumes edited by T. Provder [*4,5*] describe laboratory automation and computer applications in polymer science more generally.

Coatings and TA

In the coatings industry—limited here to commercial paints and industrial coatings—TA has proven to be a cost effective means for understanding the interrelationship between a coating's synthesis, formulation, and end-use performance [*6*]. Techniques historically important in coatings characterization can be broadly grouped under the headings of differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermomechanical analysis (TMA), dynamic mechanical analysis (DMA) and thermogravimetry (TG). Techniques such as dielectric analysis (DEA) and evolved gas analysis (EGA) have gained popularity as tools for coatings characterization as well. Although results are easily obtained using these techniques, they are grounded in complex thermodynamic and kinetic principles. Excellent overviews of the foundations, instrumentation, and applications of thermal analysis can be found in reviews by Wendlandt [*2*], Wunderlich [*7*], and Turi [*8,9*]. The International Confederation for Thermal Analysis (ICTAC) also provides an overview of TA and a list of reference articles [*56*].

[1]Associate scientist, The Glidden Company, a part of ICI Paints World Group, Glidden Research Center, 16651 Sprague Road, Strongsville, OH 44136.

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While a single TA technique may adequately characterize a research or production problem for a given system, questions often arise in the coatings industry that require several analytical techniques for adequate characterization. In fact, relying on a single characterization method could lead to serious errors in interpretation and, depending on the problem, serious financial consequences as well. The continuing development of simultaneous methods in TA underscores the value of combining techniques. They offer the advantage of simultaneous analysis of changes in physical and/or chemical properties under identical thermal conditions. There are a variety of these instruments available: examples of these "hyphenated" techniques include TG-MS (mass spectrophotometry), TG-DTA or TG/FT-IR (Fourier transform infrared spectroscopy).

Industrial applications of thermal analysis for coating characterization fall loosely into four areas:

- Product research and development.
- Problem solving.
- Quality control and quality assurance.
- Competitor products analysis.

While the results obtained using thermal analysis often focus on intrinsic properties such as component Tg's or the complex analysis of a material's viscoelastic behavior, thermal analytical methods are more typically focused on process properties and product properties. This paper provides an overview of the use of TA in the coatings industry and includes descriptions of the instrumentation, experimental conditions, and typical results.

EXPERIMENTAL TECHNIQUES

Scans were made using the TA Instruments' (formerly DuPont) 990, 9900, 2000, or 2100 temperature programmer controller. Nonisothermal studies were completed at heating rates varying from 5 to 15°C/min; isothermal temperatures will be noted as required. All scans were made under dry nitrogen or air. Each instrument was calibrated and operated using the manufacturer's recommended procedures. The typical operating conditions for each instrument are described below, with other important key experimental variables noted where necessary. A general overview of running experiments with each instrument is included at the end of each section.

DSC—Nonisothermal scans were made variously using the TA Instruments' 910 and 2910 DSCs, typically with 5.0 ± 0.1-mg samples. Materials were usually scanned twice, initially to establish uniform thermal histories and again to learn about specific physical properties. Runs were generally made at heating rates of 15°C/min between −125° and 250°C under a 50 mL/min nitrogen or air purge. In some instances, latex samples were introduced into liquid drop pans and dried in a controlled humidity chamber for a minimum of 24 h before analysis.

DSC Reaction Kinetics—Similar conditions to those described above were used, although heating rates were generally held to about 5°C per minute. Samples of unreacted material weighing about 10 mg were placed in special pans for liquid samples. In the residual heats of reaction experiments, heats of reaction were determined for samples removed from a batch reactor at 10-min intervals throughout the reaction process. The residual heats were measured under nonisothermal conditions using commercially available software. The ratio of partial heats of reaction to total heat of reaction as the polymerization progressed was given as the percent chemical conversion.

DMA—DMA scans were made variously in vertical and horizontal modes on TA Instruments' 981, 982, and 983 DMAs. All studies were completed at 5°C/min, usually under nitrogen purge. Cure studies employed either fiberglass braid supplied by TA Instruments or stainless steel mesh (Cleveland Wire Cloth & Mfg., Cleveland, OH). In cure studies, 100-μL wet samples were applied to substrates mounted in the DMA using analytical pipettes [50 mL ± 0.5% to deliver (TD)]. Isothermal temperatures were typically attained by mimicking the come-up time in an oven. For example, if a coated panel required 4 min to reach bake temperature in a production scale oven, then a similar time schedule was programmed into the DMA.

TMA—Thermomechanical and dilatometric experiments were made using TA Instruments' 942 and 943 TMAs. Scans were made at 5°C/min under nitrogen or air between about −50 and 250°C. In general, the sample was cooled at least 50°C below the expected transition temperature. TMA scans were typically made directly on coated substrates, while dilatometric experiments were completed on samples varying between 0.1 and 0.6 mm in thickness. In the penetration experiments, loads were typically about 5 g (0.05 N).

DEA—The TA Instruments' 2970 DEA and either the parallel plate or ceramic single surface sensors were used in the dielectric experiments. Parallel plate sensors were used to study thin films removed from various substrates. Ram force varied from a few newtons to 175 N depending on the coating. The ceramic single-surface sensor was used to study resins and powders. 100-μL samples were spread uniformly on the sensor and dielectric measurements recorded from 0.1 Hz through 100 kHz in order-of-magnitude increments. Heating rates were selected to ensure that an entire set of frequencies (0.1 Hz through 100 kHz) could be recorded for each 1°C increase in the sample temperature. Samples were typically scanned at 1 to 2°C/min between −125 and 200°C under nitrogen.

TGA—TA Instruments' 950, 951, and 2950 TGAs were used in the examples described here. Samples used in typical thermogravimetric experiments usually weighed between 3 and 10 mg. Scans were made at 10°C/min under nitrogen beginning at room temperature (RT) and ending at 600°C. The high-resolution thermogravimetric analysis described here was completed at 50°C/min in nitrogen at a resolution factor of 5; sample weights ranged between roughly 10 and 12 mg.

DIFFERENTIAL SCANNING CALORIMETRY

In differential scanning calorimetry (DSC), the difference in heat flow between a sample and a reference is measured under precisely controlled thermal conditions. Coatings generally possess one or more characteristic transitions, includ-

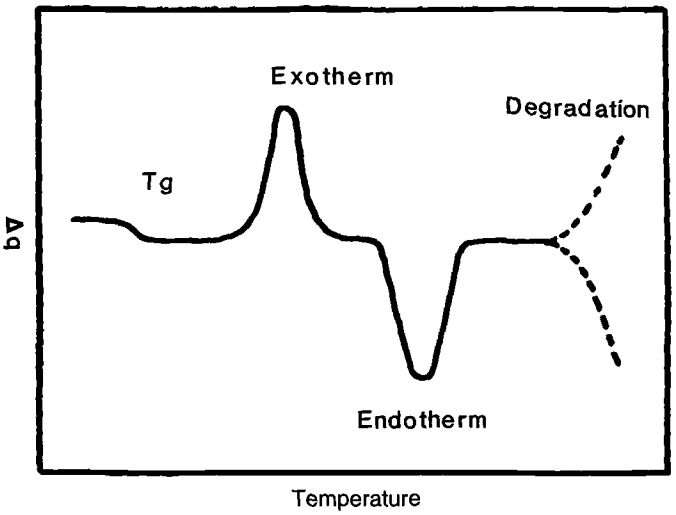


FIG. 1—Schematic DSC curve illustrating common transitions observed by DSC (Δq = heat flow).

ing (1) the glass transition (Tg) or a transition related to changes in specific heat; (2) exothermic peaks brought about by a physical process or a chemical reaction such as crystallization or a chemical process such as a cross-linking reaction; (3) narrow endothermic peaks related to fusion or melting; (4) broader endothermic peaks caused by the volatilization of low-molecular-weight materials, dissociation, or decomposition; and finally, (5) an increase or decrease in heat flow with oxidative or thermal decomposition. The results shown in Fig. 1 illustrate most of the transitions common in coatings. The DSC has a number of important uses in coatings characterization; two of the most important—Tg determination and reaction kinetics analysis—are described in more detail below.

Glass Transition Temperatures—Probably the best understood and most commonly used property of polymers, glass transition temperatures are important in virtually every phase of a coating's development and manufacture. The Tg marks a polymer's transition from an amorphous glass to a rubbery solid and defines the limits of processability for most polymers. In a nonisothermal or rising temperature DSC experiment, the glass transition coincides with a relatively sharp increase in heat flow to the polymer and a corresponding increase in the polymer's specific heat. Several techniques can be used in the assignment of a DSC Tg, including the onset, midpoint, and endpoint of the transition; in practice, the Tg is most commonly assigned to the extrapolated onset of the transition.

Sample Preparation and Tg Measurement—Measuring the glass transition temperature usually means nothing more than removing a sample from a substrate, placing it in a sample pan, and heating through the glass transition temperature in the DSC. Either of two techniques can be used to determine the Tg. When the "product" Tg (including all processing and thermal history effects) is of interest, Tg's are obtained with a single temperature sweep. Where thermal history effects are unwanted complicating factors, two temperature sweeps are used. The first sweep removes thermal history effects (for example, sample preparation or aging effects) while the second sweep gives the Tg. The latter technique works very well provided that there are no chemical changes, solvent losses, or morphological alterations during the first sweep.

Sometimes, inconsistencies in sample preparation or a seemingly unimportant detail can significantly influence the interpretation of the results—particularly when first run transitions are required. In the example below, two latexes—one scraped from a glass slide and placed in a vented pan and the other dried directly in a liquid drop pan—produced considerably different results. The samples were dried side by side in a dessicator before analysis.

The sample scraped from the glass slide shown in Fig. 2 exhibits a large endothermic peak centered around 75°C. Normally, this endotherm would suggest the loss of a volatile component or an important morphological feature. However, the results for the latex dried directly in the liquid drop pan suggest that something else is influencing the results. The heat flow curve for the latter sample exhibits no endotherm and has a Tg some 15°C higher than the sample removed from the glass slide. High-resolution videography resolved the issue, showing that the difference in Tg and the endothermic "event" was probably brought about by the softening and subsequent relaxation of the latex pieces scraped from the glass slide. What appeared as a significant morphological feature was nothing more than an artifact of the sample preparation process. In a typical two-sweep Tg measurement, this endotherm most likely would have been ignored and only the second run Tg reported, but, in studies that require the first-run data (as was the case here), the wrong conclusions could have been drawn.

Tg and Composition—Tg's obtained by DSC are also used to confirm the accuracy of Tg's calculated from additive relationships like the Fox equation [*10*]. The Fox equation and others like it are employed by coatings chemists in synthesizing copolymers to a specific Tg. Tg's obtained with these equations are based on the interrelationship of the molar or weight fraction of each monomer and their corresponding Tg's. While experimental results usually confirm the accuracy of Tg's calculated with these relationships, experimental and calculated results can deviate significantly from one another, a fact that underscores the need to verify expected results with an objective measure.

The discrepancy between calculated and experimentally obtained Tg's for four acrylic copolymers, shown in Fig. 3 and Table 1, aptly demonstrate the importance of corroborating calculated Tg's by DSC. In this example, the Tg's determined by DSC are much lower than the Tg's obtained using the Fox equation. Close examination of the DSC heat flow curves gives outstanding clues about the character of the polymers being analyzed. Compared to a typical Tg, the transitions in Fig. 3 are very broad—covering some 40 to 50°C—and quite shallow, falling less than 0.1 cal/s/g from beginning to end. The character of the glass transition region in a typical DSC is quite different. The temperature range of this region is usually no more than about 25°C wide and usually drops more than 0.5 cal/s/g over the Tg range. The differences between assigned and calculated Tg's probably stem from the combined effects of monomer sequence distribution [*11*] and end group effects related to the relatively low molecular weight

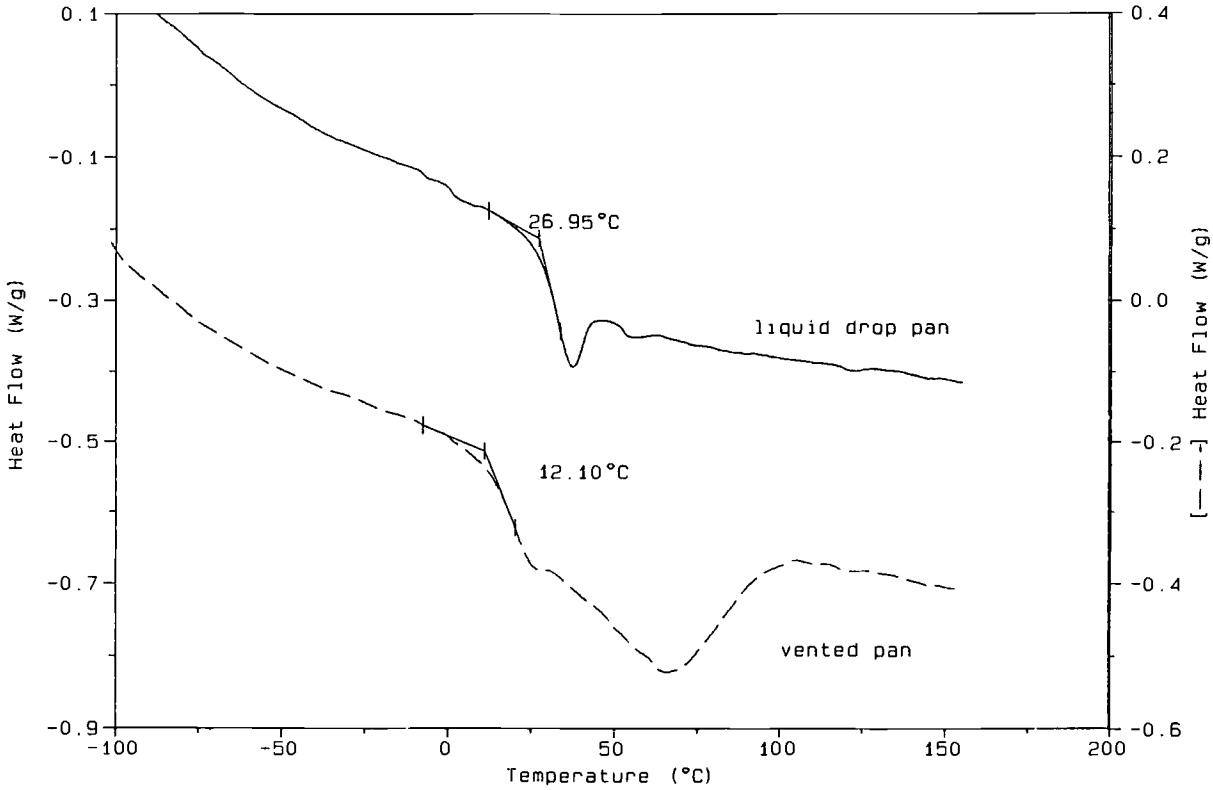


FIG. 2–Characteristics of the glass transition in identical latexes prepared by different methods.

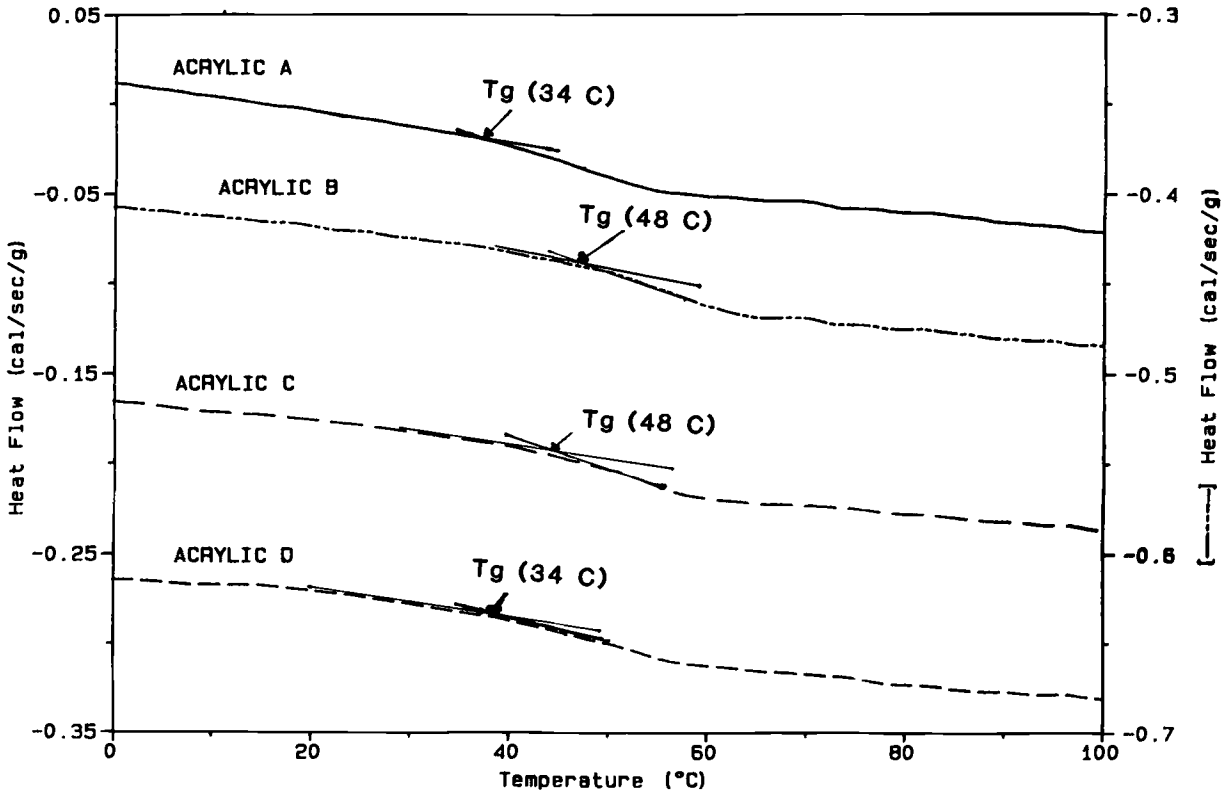


FIG. 3–Glass transition temperatures for four acrylic copolymers.

TABLE 1—Calculated[a] and experimentally (DSC) determined Tg's (°C) for four acrylic copolymers.

Acrylic Copolymer	DSC Tg	Fox Tg
A	34	60
B	48	65
C	48	70
D	34	75

[a]Tg's were calculated using the Fox equation.

[*12*] of these copolymers. The polymers used in this experiment were all low-molecular-weight tetramers (number average molecular weight < 5000) composed of various combinations of methylated and butylated acrylics. Van Krevlan [*1*] provides a more comprehensive overview of polymer properties which could have an influence on the assignment of the glass transition temperature.

REACTION KINETICS

A number of techniques have been developed for measuring the kinetic parameters of chemical reactions from DSC data. The primary advantage of these techniques over traditional wet chemical techniques is their speed and simplicity. Research in reaction kinetics analysis by DSC includes studies focused on isothermal techniques [*13–15*], nonisothermal (also known as temperature variant, rising temperature) or dynamic methods [*16–17*] and multiple scan methods [*18–19*]. Each method uses the rate of heat evolution as the computational parameter, implicitly assuming that the reaction is not autocatalytic, has one rate-limiting step, and is unaffected by changes in reactant concentration or volume. The validity of kinetic data obtained using nonisothermal procedures has been the source of considerable technical effort and discussion in the literature (see, for example, Refs *20* and *21*).

Nonisothermal reaction kinetics analysis plays an important role in the characterization of coatings. Differential methods based on the work of Borchardt and Daniels [*16*] are the most commonly used in obtaining reaction kinetics parameters by DSC. These methods assume that the heat evolved during a reaction is proportional to the extent of reaction. The order of reaction, n, the activation energy, E (kJ/mol), and the Arrhenius constant, A (s^{-1}), are determined using an equation based on a general nth order rate expression

$$\frac{dF(t,T)}{dt} = k[1 - F(t,T)]^n \quad (1)$$

where $F(t,T)$ is the fractional extent of conversion [partial heat of reaction ΔH (t,T) divided by the total heat of reaction H_0], k is the rate constant, t is time, and T (K) is the absolute temperature. The temperature dependence of the rate constant is given by the Arrhenius expression

$$k = A \exp(-E/RT) \quad (2)$$

where R is the ideal gas constant (J/mol K). The methods used here have been described in detail elsewhere [*22–23*].

In nonisothermal kinetics experiments, autocatalytic reactions and first-order reactions are virtually indistinguishable because both reactions produce a uniform, monomodal, exothermic peak as the experimental temperature increases. The only way to determine the nature of the reaction mechanism is by running an isothermal experiment. An isothermal experiment will clearly differentiate between the two reaction types because the exothermic peak marking the maximum rate of reaction will occur at very different points, depending on the nature of the reaction. In a reaction that obeys first-order kinetics, this peak will occur immediately after reaching the isothermal temperature. In an autocatalytic reaction, the maximum rate of reaction—and therefore the peak maximum—occurs well after reaching the isothermal temperature.

Epoxy-Amine Reaction Kinetics

Maximizing the efficiency of a reactor and minimizing raw material waste in a chemical reaction depends inherently on knowing how a reaction proceeds and, more specifically, how long the reaction takes to reach completion. Unfortunately, measuring the rate and degree of conversion in reactors holding hundreds or even thousands of gallons is a prohibitively expensive process during product scale-up. Small-scale laboratory DSC experiments representative of a production reaction can significantly reduce reactor time and process costs. Modeling the extent of reaction using DSC kinetics analysis can further shorten the development process and can be used to predict the extent of reaction under widely varying temperatures and reaction times. In the example that follows, these techniques were used to optimize reactor time and improve productivity in manufacturing. The reaction involved a typical diglycidyl ether of bisphenol A (DGEBPA) epoxy and an amine.

In this example, chemists arbitrarily placed the time to form an epoxy adduct at 8 h, a substantial manufacturing cost when considering reactor time and labor. However, predictions based on nonisothermal DSC reaction kinetics showed that the reaction should actually reach completion much faster than 8 h. In fact, DSC reaction kinetics parameters (n = 1.1, E = 72.0 J/mol, and ln A = 19.2) indicated that the process should take about 2 h under the specified polymerization conditions. These results were then corroborated by measuring the residual heats of reaction (see experimental for details) observed in small samples taken from a 100-gal reactor. Figure 4 compares predicted conversion with the residual heats of reaction measurements. While neither method was extended to show the actual time required to reach 100% conversion, extrapolation to 100% conversion indicates the reaction should reach completion after about 2 h. Table 2 compares selected data from Fig. 4 at specific reactor times. These results show that the reaction reached a higher level of conversion (based on DSC residual heats) in the manufacturing process (88%) than predicted by DSC (67%). Nonetheless, the extrapolated end-point from the DSC kinetics analysis—although a bit high at 2.5 h—is much better than the 8-h reactor time set arbitrarily by the chemists.

The discrepancies between the measured and calculated degrees of conversion are probably related to competing side reactions that could occur in DSC experiments (i.e., at elevated temperatures) but not during manufacturing and also to the vast difference in the reaction conditions: DSC kinetics

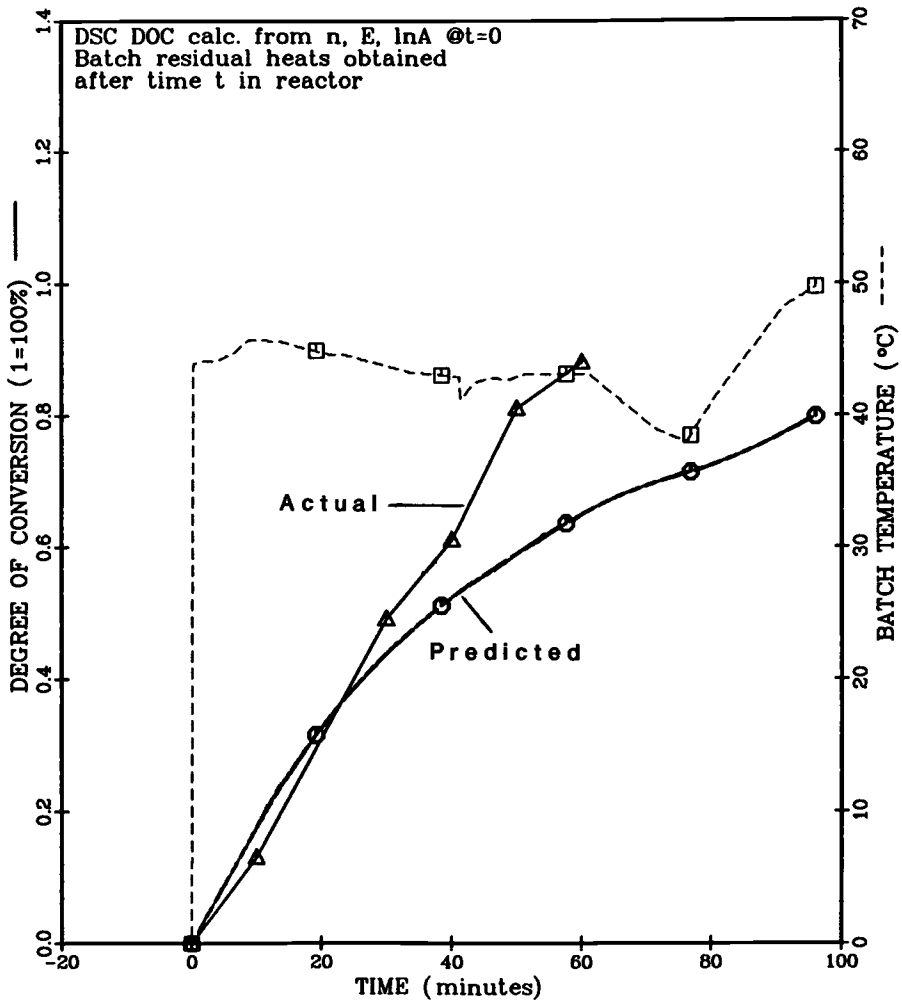


FIG. 4—A comparison of actual and predicted degree of conversion in an epoxy-amine reaction. The predicted degree of conversion at each point was based on DSC kinetics analysis, while the actual degree of conversion at each point was based on the residual heat of reaction on samples removed from the reactor.

analyses were made using fresh 5-mg samples, while the residual heat studies were made with samples taken from a 100-gal reactor.

Coatings Characterization by DSC

Sample Preparation: The materials typically analyzed in the coatings industry can come as either solids or liquids. Solids require little special preparation; they just need to fit in the pan and, most importantly, remain very flat on the bottom of the pan. Liquids are another matter and usually require a special container for analysis. No matter what the form, limit your sample size to somewhere between 5 and 10 mg. Large samples (>10 mg) may not heat uniformly, with the outer layers heating more rapidly than the center of the sample. You can also get results with samples in the 1-mg range, but using smaller masses can reduce resolution. For a more accurate assignment of the Tg, use high sample weights (ca. 20 mg) and slow heating rates (1°C/min).

Either open or closed pans can be used. We prefer closed pans with perforated (use a fine needle) lids. Lids help keep the DSC oven or cell clean; the perforations prevent pressure buildup caused by solvents or low-molecular-weight reaction products. Many others use only open pans.

Liquid paint and latex samples are treated somewhat differently in that they are placed in open pans (especially designed for liquids) and allowed to dry (24 h minimum) before analysis. This approach prevents the development of artifacts that sometimes occur when a dried sample is scraped from a substrate and placed in the pan.

TABLE 2—Chemical conversion obtained from residual heats of reaction and simulations using DSC kinetics parameters.

Reaction Time, min	Actual % Conversion	Predicted % Conversion
0	0	...
10	14	19
20	31	33
30	49	43
40	61	53
50	81	61
60	88	67

Purge gas: The selection of purge gas depends on your objectives. High-purity dry nitrogen (99.99%) is typically used. It offers low cost and reasonably good heat transfer. Argon, another frequently used gas, improves heat transfer and the resolution of the analysis but at increased cost. Purge rates vary with the instrument.

Temperature Range and Heating Rate (β): Start each temperature sweep at about −125°C and end at least 50°C above the Tg. This temperature range will include any transitions in typical coating systems that could affect performance. If you know the Tg of your sample and you are unconcerned about ancillary transitions, use the 50/50 rule: start runs 50°C below the Tg and end them at least 50°C above the Tg, making sure that the sample has time to equilibrate at the starting temperature.

The important consideration in selecting a heating rate is heat transfer and the steady state conditions in the sample. For routine analysis, a 15°C/min heating rate offers a good compromise between run time and resolution. Keep in mind that high heating rates can produce thermal lag in the sample and tend to broaden transitions. And, when there are two or more transitions, they tend to run together. Slower heating rates are usually used where there is a need for high resolution. But, when time is not a concern, slower rates are always preferable. There are also instances, for example film formation experiments, where isothermal temperatures are necessary. Choose an experimental temperature slightly higher than ambient, say 30°C, for controlled room temperature experiments.

Thermal History: In most analyses, the sample should be analyzed twice. In unreactive systems, the first sweep erases any effects of the sample's previous thermal history and establishes a uniform baseline for each sample—this is especially important in comparing a series of samples.

In reactive materials, analyze through the cure temperature and allow for the reaction to reach completion. Determining the proper temperature range may require some "scouting" experiments. In isothermal cure studies at elevated temperatures, try to simulate bake conditions. Select an initial heating rate that approximates come-up time for a substrate in an oven and add enough time at the bake temperature to match the typical oven "dwell" time.

Data Collection: In non-isothermal or rising temperature experiments, try to average between two and eight data points per degree Celsius increase, depending on the experimental objectives. Higher heating rates require higher data-collection rates to obtain the same resolution. Note that high data-collection rates at slow heating rates can produce large data files. Data collection for isothermal studies must be tuned to the time required for an event to occur. Fast events would require high data collection rates; slower events would require correspondingly lower rates.

DYNAMIC MECHANICAL ANALYSIS

DMA measures the viscoelastic response of a material under a periodic load. Dynamic mechanical analysis represents one of several methods for mechanical properties analysis [*24–26*] providing a valuable link between chemistry, morphology, and performance properties [*27–29*]. The DMA's applications range from the measurement of bulk viscoelastic properties to the sophisticated analysis of the kinetics of the cross-linking reaction. Depending on the geometry of the clamps and the instrument's design, the oscillatory load applied may be in flexure, tension, compression, or torsion; sample oscillation may be either at resonant frequency or at fixed frequency. These tests simultaneously produce elastic modulus and mechanical loss or damping values. Modulus values (flex, Young's, shear, bulk) provide an indication of material stiffness, while mechanical damping correlates with the amount of energy dissipated as heat during the deformation of the material. In tensile mode, these instruments can provide creep and stress relaxation data and can even be used in WLF [*30*] transformations (see Ref *30*).

In the coatings industry, DMA is broadly applicable to the study of film properties [*31*] and particularly important for cure process studies [*32–34*]. Another important application of the instrument involves characterizing paints after application and the film-formation process. A detailed overview of the use of DMA in thermoset cure studies is provided later in the chapter. Figure 5 illustrates the typical viscoelastic response for a generalized polymer coating. In this example, the glass transition temperature corresponds to a large decrease in modulus beginning near 25°C and a peak centered at about 70°C on the loss modulus curve. In noncrystalline polymers, transitions found below the Tg or in the glassy state are usually associated with the molecular motion of the backbone or small groups pendant to the main chain. At the same time, modulus values in the region above the Tg—the rubbery state modulus—impart information about a material's molecular weight or degree of cure, depending on the material. In thermoplastic materials, increasing rubbery state modulus values usually indicates increasing molecular weight. In thermoset materials, increasing rubbery state modulus values indicates higher cross-link density. A more complete description of the dynamic mechanical properties can be found in monographs by Nielsen [*24,25*] and Ward [*26*].

Synthetic Variables and Morphological Character

One of the strengths of dynamic mechanical analysis lies in its utility for resolving the effects of relatively minor changes in formulation or processing. Differences in these variables (usually) induce easily discernable changes in the viscoelastic properties of a polymer. For example, the materials shown in Figs. 6*A* and 6*B* are both epoxy acrylic coatings used in food packaging. While the coatings are made of virtually the same materials, their chemistries and processing conditions are different.

The presence of two glass transitions in the relative modulus curves in these graphs indicates that both coatings are heterogeneous systems. However, these curves give little indication as to whether the epoxy or the acrylic is the continuous phase. A comparison of the damping peaks reveals a difference in the peak intensity (or peak height) of the two transition regions. In filled systems, polyblends, and grafted systems, the intensity of the damping peak gives a rough estimate of the concentration of the components and an indication of which phase is continuous. The greater the concentration, the larger the damping peak and the more likely that phase is continuous [*24*]. In Fig. 6*A*, the epoxy phase peak at roughly 130°C has considerably greater magnitude than the

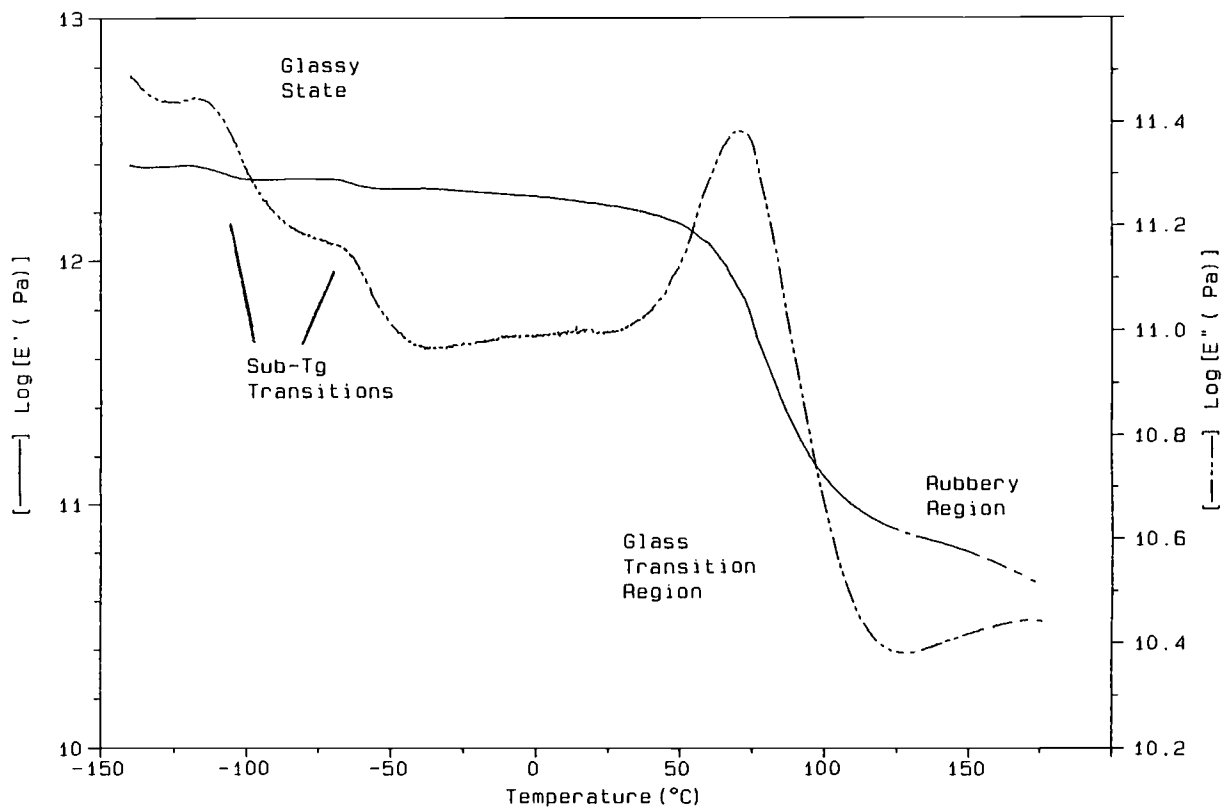


FIG. 5–Typical viscoelastic response in polymeric systems, log relative modulus (*E'*) and log relative loss (damping, *E"*).

one assigned to the acrylic and so would be the continuous phase. In Fig. 6*B*, the opposite is true. In this case, the acrylic phase centered near 90°C is continuous while the epoxy is the dispersed phase.

Aside from the information on morphology, these curves also give us information on the relative miscibility of these systems. If these two polymers were totally miscible, both the modulus and damping curves would have only one transition. Since there are two, it is clearly a two-phase system. Careful scrutiny of the two systems reveals that the peaks in Fig. 6*B* fall much closer together than those in Fig. 6*A*. This strongly suggests that the conditions used to produce the material in Fig. 6*B* produce a more miscible polymer.

Coatings Characterization by DMA

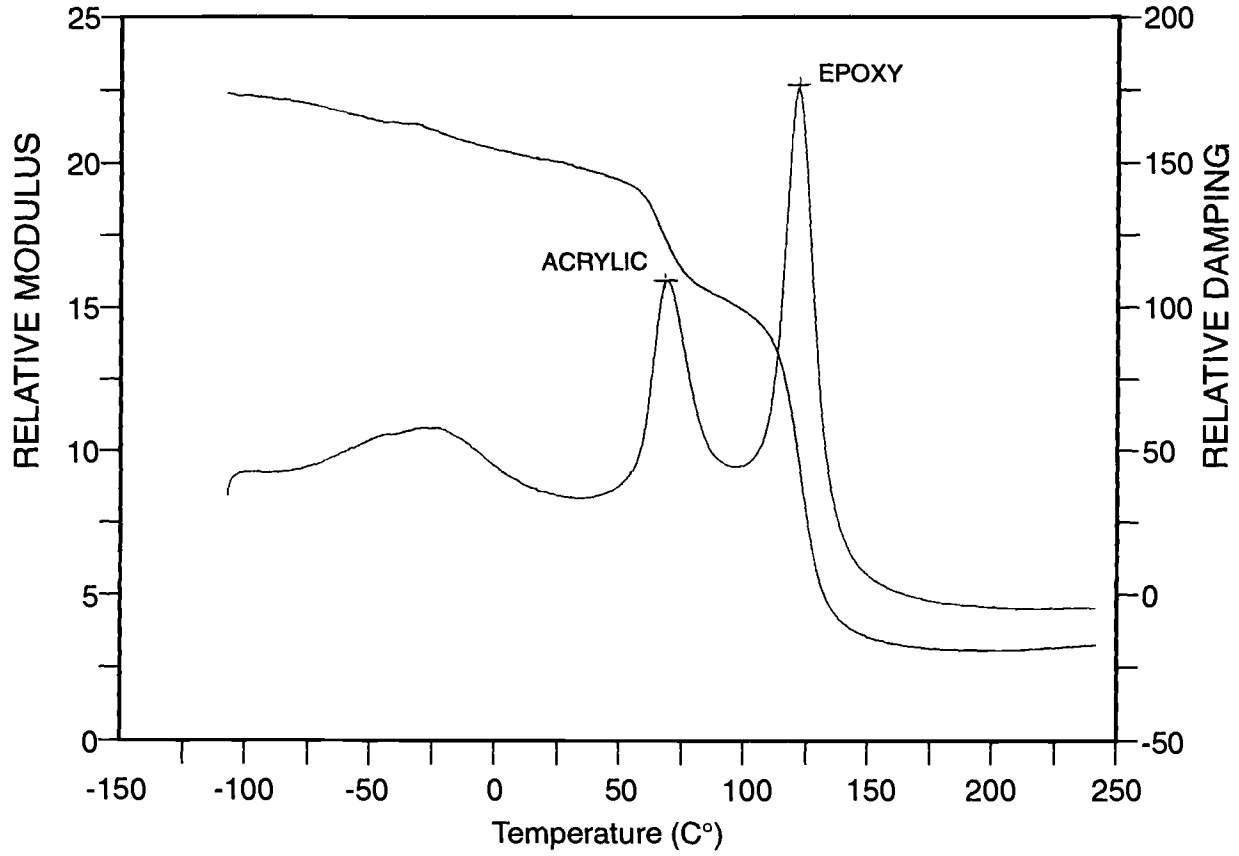
Dynamic mechanical analysis can be one of the most demanding and least forgiving of all the TA techniques. It's vitally important to spend time learning the instrument's idiosyncrasies before putting complete faith in the viscoelastic measurements the instrument produces. Each commercial instrument offers unique sample mounting geometries and usually offers a variety of experimental approaches. Regardless of the experimental approach, take the time to run a half-dozen experiments using identical experimental conditions so that you can better understand the range of results to expect under a given set of experimental conditions.

Sample Preparation: There are several approaches to forming free films for DMA investigations. These include coating low-energy surfaces like PTFE (Teflon) or polypropylene or coating thin aluminum sheet stock, allowing sufficient time for film formation, and dissolving the aluminum away with an alkali. Sample dimensions must always conform to the limits prescribed by the instrument manufacturer; wherever possible, however, sample thickness should closely approximate the thickness of the coating film in the field. In this way, test results will more closely represent those found in realistic end-use conditions.

Unfortunately, free films are not always a viable experimental choice. In those instances, coated substrates, e.g. very thin stainless steel shim or fiberglass braid, are often used. Although constitutive equations are available for obtaining absolute mechanical properties values from coated substrates, usually only relative measurements are made using this approach.

To insure uniform thermal histories, prepare specimens in a controlled environment. Small differences in film-forming temperature or humidity in replicate runs on the same coating can make it appear as if two different coatings had been tested. Well-controlled and consistent sample preparation allows the additional advantage of comparing results from tests made over many months or years without concern about differences in film-forming conditions.

Heating Rate: Undoubtedly, one of the most, if not the most, important consideration is choosing proper heating rates. While most instruments make rapid heating rates available (some manufacturers claim 200°C/min), it is wisest to choose very slow heating rates—at most, heating rates of about 1 or 2°C/min. Slow heating rates allow the entire sample to equilibrate to temperature change and thereby improve the reliability of transition temperature assignments. When



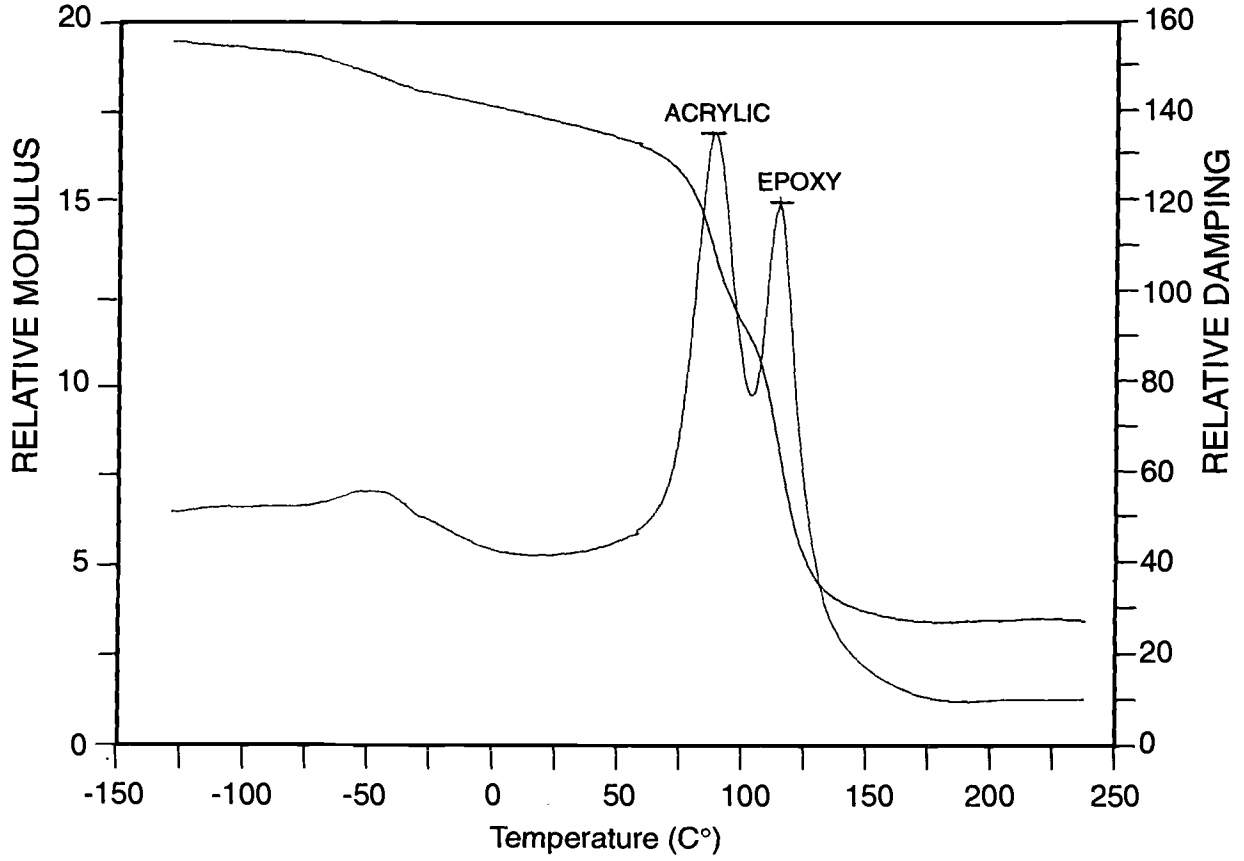


FIG. 6–Dynamic mechanical properties of epoxy/acrylic copolymers.

time allows, the best way to control thermal lag in the sample is by using step-change experiments. This kind of experiment combines slow heating rates (1 to 2°C/min) and isothermal "steps" (1 to 5 min), which allow the sample to equilibrate before heating to the next isothermal step. For thin coatings, shorter isothermal periods (1 to 2 min) are satisfactory, while thicker samples require longer (e.g., 5 min) isothermal steps.

Strain or Oscillation Amplitude and Frequency: In general, the greater the applied stress, the longer the relaxation time. Ideally, the sample should come close to full recovery from one applied stress before the next one begins. This means the experimenter should choose well-matched amplitudes and frequencies. For example, choosing a large mechanical deflection means that the time between the applied stresses should be longer. Conversely, higher-frequency experiments should have correspondingly smaller applied stresses. The proper relationship between the test frequency and oscillation amplitude will ensure that the sample has come close to mechanical equilibration between "events." In most instruments, the amplitude of the deflection is based on controlled strain. In these instruments, the maximum applied strain should be at 0.1% or less. This is particularly important in filled systems (like coatings), which will exhibit nonlinear responses more readily than unfilled systems.

Because mechanical relaxation times vary widely in polymers, there are no specific rules governing the selection of oscillation amplitudes and test frequency. As a general rule, oscillation amplitudes of a few tenths of a millimeter at 1 Hz are commonly accepted practical "standards." In very hard (brittle) or very soft materials, however, it's generally best to perform a controlled stress (stress relaxation or creep) experiment rather than an oscillating stress experiment.

Gas Flows: Where possible, apply a uniform gas flow. We arbitrarily set our gas flow rates so that gas content in the oven chamber "turns over" about once every 1 to 2 min. Since the size of these chambers varies considerably, flow rates will, too. If in doubt, use the manufacturer's recommended purge rates.

THERMOGRAVIMETRY (TGA)

Thermogravimetry describes an analytical technique used to monitor a change in sample mass as a function of time or temperature. Depending on need, either isothermal or nonisothermal experiments are possible; nonisothermal experiments—where the sample temperature changes at a linear rate—represent the most frequently used mode. In coatings technology, the instrument is most frequently applied in compositional analysis, e.g. nonvolatile content, and for studies of thermal stability. The technique can also be applied in studies of accelerated aging, decomposition kinetics, and oxidative stability.

In recent years, improvements in commercial instrumentation have enhanced resolution to about 0.05 mg. The primary differences between the types of commercial instrumentation center on the furnace type, the quality of the software, the control of gas flow, and the sensitivity of the microbalance. In addition, high resolution TGA and a robotic system are also available. Coupled with a mass spectrometer, gas chromatograph, or FT-IR, TGA becomes a powerful analytical tool combining both physical and molecular probes in a single technique.

Compositional Analysis—From time to time, performance properties will change because a material supplier makes changes in the formulation or manufacture of a product. Although the supplier may not recognize it, relatively minor changes in a material can engender major changes in a coating's performance, sometimes with a monetary consequence. Thermogravimetry provides one means for learning more about the composition of a material and when problems arise helps maintain acceptable performance. In this example, an unusual "settling" problem was traced to a subtle difference in the composition of a wax used in the paint formulation.

Other than a difference in the melt enthalpies, studies by DSC and conventional TGA (ramped at 10°C in N_2) analysis revealed that these waxes were virtually identical. However, when characterized using high-resolution thermogravimetry, small but significant compositional differences between the good (A) and suspect (B) samples became apparent.

Figure 7*A* shows the relative weight change in these materials as they decompose to carbon-char. Weight loss follows roughly the same path, regardless of the lot tested: beginning with a small step near 175°C, weight loss proceeds through a major step at around 300°C and ends with another small step between 450 and 500°C. The derivative (%/°C) curves shown in Fig. 7*B* offer the best illustration of the differences between lots. Each of the peaks in this figure represents a different decomposition step or combination of steps. If these materials were truly the same, the shape of the peaks and the peak temperatures would be virtually identical, but these materials possess several differences. Most notable are those associated with the peak between 250 and 300°C: the shape and position of this peak varies significantly. Working closely with the wax manufacturer, these results helped to identify a processing error and led to narrower manufacturing specifications. Earnest [*3*] provides a more detailed overview of thermogravimetry and its application to compositional analysis. Table 3 describes the differences in the thermal behavior in these lots of wax.

Volatile Organic or Moisture Content—With ever-tightening regulatory requirements, measuring the moisture or volatile organic content (VOC) has become increasingly important in the coatings industry. Figure 8 shows the relative nonvolatile content of two polystyrene latexes. Beyond simple measurements of volatile content, the technique is an excellent way to determine the amount and rate of evolution of decomposition products.

Thermal Stability—TG is also used widely to monitor the stability of polymeric coatings. Figure 9 shows that the long-term degradative stability of a coating based on a vinyl-ester resin was superior to a similarly formulated coating based on an epoxy resin. The information shown here was useful in establishing the cost-effectiveness of the vinyl-ester system.

Coatings Characterization by TGA

Sample Preparation: The materials typically analyzed in the coatings industry can come as either solids or liquids. Neither solids nor liquids require special preparation; they just need to fit in the pan. Like DSC, limit your sample size to

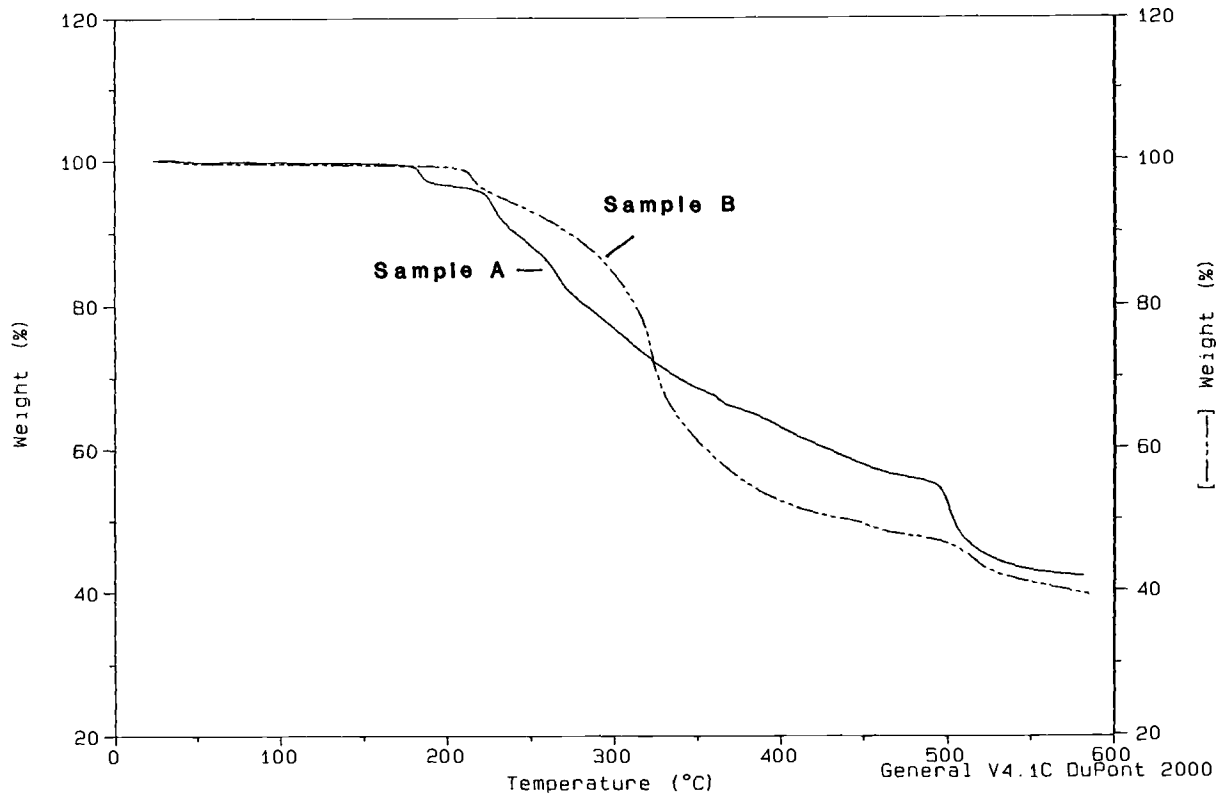


FIG. 7*A*–Weight loss curves for waxes with ostensibly identical compositions.

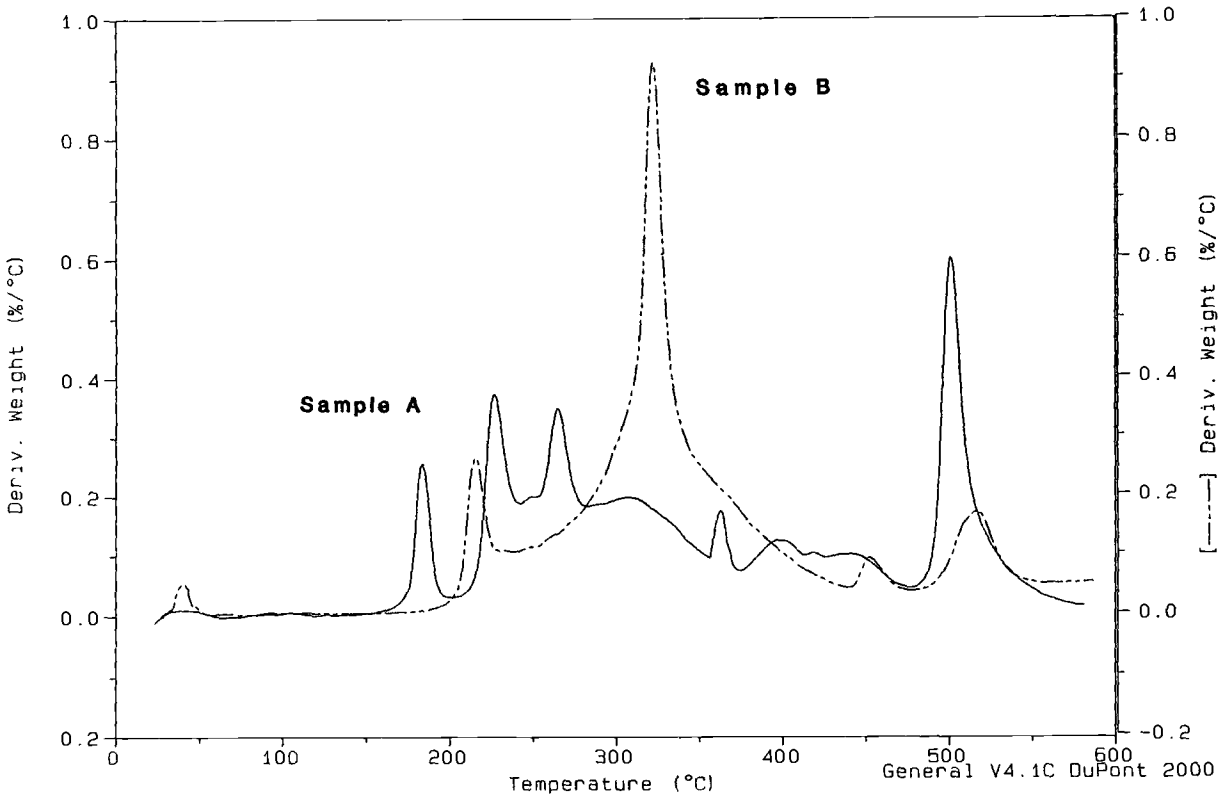


FIG. 7*B*–A comparison of the weight loss derivatives for the weight loss curves shown in 7*A*.

TABLE 3—Wax melt characteristics and decomposition characteristics.

Sample	Condition	T_m − 1(°C)	Total ΔH_m	Decomposition Onset-1, °C	% Char
A	Control, dry	87.7	75.7	172	38
B	Suspect, dry	87.4	46.1	150	43

NOTE: T_m = melt temperature.

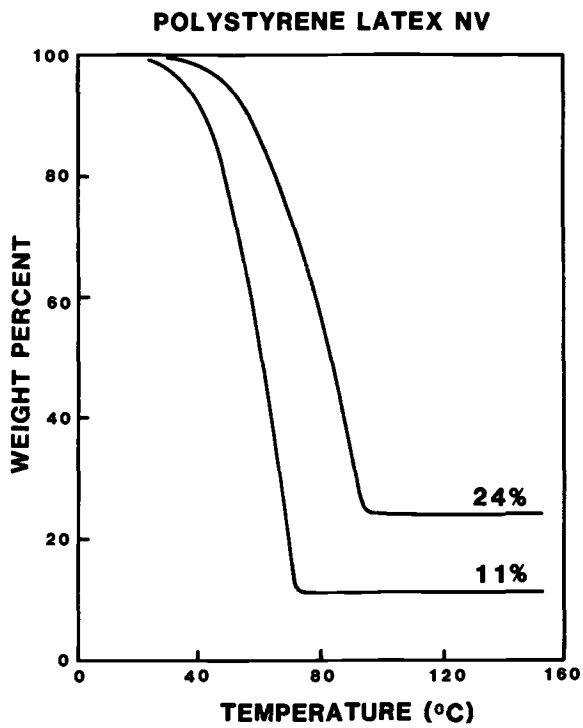


FIG. 8–Polystyrene nonvolatile (NV) content measurement obtained through TG.

somewhere between 5 and 10 mg. Large samples (>10 mg) may not heat uniformly, with the outer layers heating more rapidly than the center of the sample. For solids, the physical form of the sample is very important to the resolution of the test results. If the surface area is large, for example a powder or highly divided solid, then higher masses—as much as 40 mg—may be used without significantly reducing the sensitivity measurement. Choose the mass of a liquid sample based on the amount of solid material present, for example, use at least 10 mg of a liquid containing 50% solids. Beyond sample considerations, be aware that both aluminum and platinum—metals which are used in a typical TGA pan—can occasionally catalyze a portion of the decomposition process in some materials.

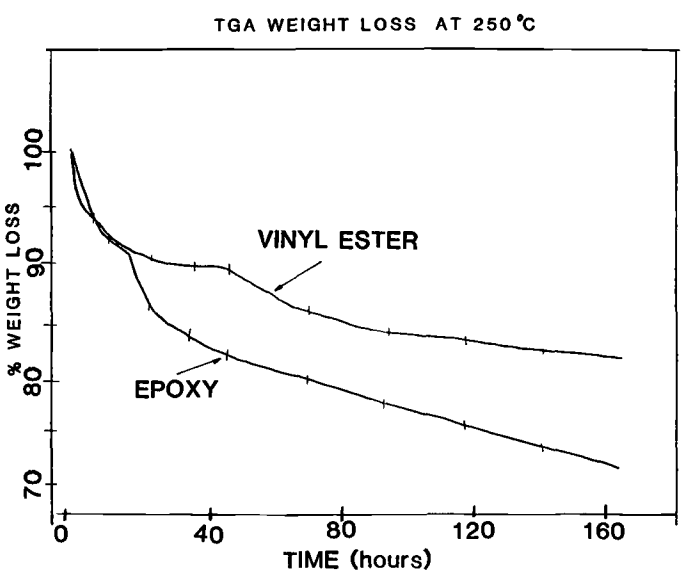


FIG. 9–Thermal stability of vinyl-ester resin.

Purge gas: Like DSC, the selection of purge gas depends on your objectives. High-purity dry nitrogen (99.99%) is typically used. It offers the benefit of low cost and reasonably good heat transfer. Argon, another frequently used gas, improves heat transfer and may improve the resolution of the analysis but only at increased cost. In some instances, you may want to control the humidity of your purge gas. A simple, low-cost method involves bubbling the purge gas through DI water in a bubble tube and running the effluent into the instrument. Relative humidity values can reach 80% using this approach. Purge rate requirements vary with the instrument.

Temperature Range and Heating Rate (β): In most compositional analyses, our experiments are run between room temperature and 600°C. This temperature range suits most coating systems because, as a rule, polymers (coating binders) usually begin to decompose somewhere between 250 or 350°C and are gone by 450°C. When running liquids, pay very close attention to the instrument's set-up time before it begins to collect data. In highly volatile materials, as much as 10% of the volatile material can be lost before the first data point is collected in the experiment. The difficulties with interpretation in this situation should be obvious.

The most important consideration in selecting a heating rate for your experiments is heat transfer and the steady-state condition of the sample. For routine analysis, a 10°C/min nonisothermal temperature ramp offers a good compromise between run time and resolution. Keep in mind that high heating rates can produce thermal lag within the sample, which in turn will broaden transition regions. In instances where a sample exhibits two or more weight loss transitions, they will tend to run together at higher heating rates. Slower heating rates are usually used where there is a need for improved resolution and run time is not a concern. Where isothermal temperatures are necessary, choose an experimental temperature most representative of the end use requirements.

A few instrument vendors offer "high or enhanced resolution" capabilities, a technique which, in essence, combines the virtues of a rising temperature experiment with the benefits of an isothermal experiment. Whatever the manufacturer's recommendation, make certain that the gas flow rates are *identical* for each part of your experiment. Analyzing the same sample with even small variations in gas flow (less than 5 mL/min) can produce dramatic changes in the weight loss curves or the weight loss derivative curves. In fact, one mate-

rial can appear to be two simply because of differences in the purge gas flow rate. These differences occur because the degradation mechanism is sensitive to temperature and holding the sample under near isothermal conditions can amplify a mechanistic step that would normally play a minor role in a standard rising temperature experiment. All of these precautions serve to emphasize one important fact: the experimenter must have a good grasp of the chemistry of decomposition when performing these experiments. Otherwise, he runs the risk of misinterpreting the results obtained for the decomposition process.

Data Collection: Try to average between two and eight data points per degree Celsius increase, depending on the experimental objectives. Higher heating rates require higher data collection rates in order to obtain the resolution obtained at lower heating rates. In some commercial instrumentation, the data collection rate can be varied from low to high at various steps in the experimental procedure. Note that high data collection rates at slow heating rates can produce large data files (using valuable disk space!) while yielding little or no improvement in the resolution of the data.

THERMOMECHANICAL ANALYSIS (TMA)

Thermomechanical experiments measure changes related to sample dimension as a function of time or temperature. These changes depend on both viscous (energy dissipative) processes and elastic (energy storing) processes within the material. Daniels [*35*] linked thermally dependent changes in dimension with various kinds of molecular motion: changes in dimension correlate with chemical reactions, lattice vibrations, changes of state, the glass-rubber transitions, changes in crystalline structure, or some combination of these phenomena. Riga and Neag [*36*] and Earnest [*37*] provide a thorough review of thermomechanical techniques and application in materials science.

The techniques associated with TMA are broadly applicable in materials science and are used in characterizing liquids, polymers, and inorganic materials. In practice, TMA is most commonly used in assigning transition temperatures or determining the coefficient of linear thermal expansion (α) by linear dilatometry. Descriptions of thermomechanical analysis (TMA) generally include linear dilatometric techniques because the same instrument can be used for thermomechanical and thermodilatometric experiments. When changes in sample dimensions are measured with a negligible load, the technique is more properly referred to as linear thermodilatometry (TDA). Depending on the experimental objective, any one of several probe types may be used.

TDA is typically applied in studies of ceramics, glasses, and metals—materials that exhibit a primarily elastic response (particularly for α)—or for determining glass transition temperatures (Tg) in polymeric materials. Dilatometric experiments are usually applied over a range of temperatures representative of the product's end use, but may begin near absolute zero and reach as high as 2500°C [*35*]. Thermomechanical analysis is most often applied in characterizing polymers or composites (e.g., most coatings), where the viscoelastic properties of a substance often dominate the material response. Thermomechanical studies usually employ a narrow range of experimental temperatures, typically falling between −175 and 850°C.

Instrumentation—The kind and quality of information obtained from a thermomechanical analyzer depends primarily on the arrangement of the sample and probe type. The penetration mode is probably the most commonly used arrangement in TMA and is usually used in assigning transition temperatures, such as the glass transition temperature or softening point temperature, in polymeric materials. In this mode of operation, substrate effects become increasingly important as the sample thickness decreases. This is particularly true in the analysis of thin films and coatings [*38*]. Tension tests are often used in characterizing the properties of thin films. In fact, improvements in instrumentation, particularly in controlling the applied force and fully automated operation, make possible the characterization of more fundamental viscoelastic properties such as creep and stress relaxation. These improvements have also increased the resolution of these instruments considerably. The resolution of these instruments ranges from about 500 nm in first-generation commercial instruments (ca. 1975–80 and earlier) to claims of less than 5 nm in second-generation instruments.

Dilatometry—This method has broad applicability in coatings technology, such as in determining the coefficient of thermal expansion (CTE). It is particularly valuable in failure analysis. For example, mismatches in CTE appear to play a role in the failure of two-coat systems such as gel coats.

Gel coats are polyester/styrene systems that are sprayed directly onto a mold surface and allowed to advance to a tack-free state. A fiberglass mat is then placed onto the partially cured gel coat and a reinforcing laminating polyester resin applied to the fiberglass mat. The laminate is removed from the mold after reaching optimum cure under ambient conditions. If the gel coat or laminating resin is improperly formulated or undercured, differences between the CTE values may be large enough to cause delamination at the interface.

Ideally, the CTE values for the members of the part should be the same or only slightly different. In this instance, however, the differences in CTE values shown in Table 4 led to delamination and the eventual failure of the part. Subsequent analysis of residual heat of reaction by DSC showed that the gel coat was improperly cured. Inadequate cure led to appreciable differences between the CTE values of the gel coat and laminate, and ultimately, to the failure of the system. Figure 10 provides a comparison of the CTE curves for the gel coat and polyester laminating resin.

TABLE 4—Gel coat and laminating resin CTE values (PPM/°C).

Material	No. of Runs	Avg CTE	Standard Deviation	Range
Gel Coat	4	5.0	0.2	5.0–5.3
Laminating Resin	5	5.9	0.1	5.8–6.1

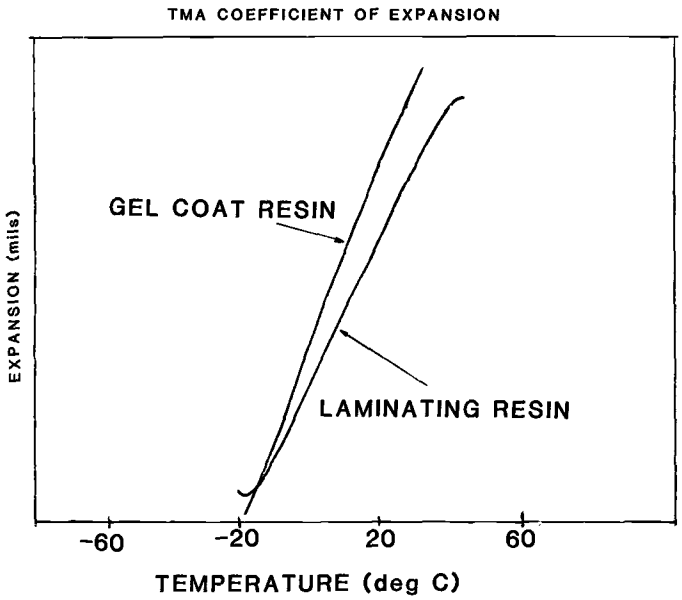


FIG. 10—A comparison of the CTE curves for the gel coat and polyester laminating resin.

Thermomechanical Analysis

Softening point temperatures (SPT) and total probe displacement obtained using thermal mechanical analysis provide valuable insight into a coating's performance, particularly in comparing the relative degrees of cure in production materials. For example, when cure levels in two container coatings were compared—one of which failed QC tests after manufacture—TMA results strongly suggested that the failed coating was undercured. The TMA results in Table 5 show that the failed coating had a lower softening point temperature and greater total displacement than the coating that passed. Rebaking the failed coating led to an increase in SPT and a decrease in probe penetration. While the changes in SPT and probe displacement indicate an improvement in performance, they still failed to match those of the coating that passes the QC test. Intentionally undercured coatings yielded similar results, strongly suggesting that the coatings that passed reached a higher degree of cure than the coating that failed. Perhaps more importantly, these materials were characterized directly on the container substrate, indicating the TMA's value in situations not amenable to characterization using more routine analytical methods.

Coatings Characterization by TMA

Sample Preparation: Sample preparation requirements vary depending on the test mode, usually either force/deflection (penetration) or dilatometric experiments. Either free films or coated substrates can give excellent results. While free films are probably best—provided that they lay flat and retain their shape during the experiment—it's usually more practical to run TMA experiments with coated substrates. If you use a coated substrate, pay close attention to sample thickness, the dimensional stability of the substrate during the experiment, and the size of the sample in relation to the probe tip. The larger the sample in relation to the probe tip, the better.

Substrates, like the coating, can change with experimental conditions and consequently influence experimental results that an experimenter might attribute to coating properties alone. The best way to avoid substrate effects is to increase the thickness of the sample. Ideally, samples should be about 500 μm (20 mils) thick, but films this thick are rarely found in any application. Moreover, increasing the thickness of the sample may improve resolution at the expense of validity. In practice, films measuring 20 μm (about 1 mil) will yield excellent quantitative results. In general, if you can make the sample thicker without compromising the validity of the results, you should. The need for thick samples doesn't mean that thin samples may not be tested. In fact, significant *qualitative* results can be obtained at film thicknesses as small as 5 μm provided that the sample preparation conditions are extremely well controlled.

If you have doubts about potential substrate effects, analyze the uncoated substrate and try to determine if the substrate will contribute to changes in the TMA's response. Some software packages will allow you to subtract baseline effects from the total response of the coated substrate. As with the DMA, ensure uniform thermal histories by preparing specimens in a controlled environment.

Heating Rate: For most applications, use heating rates around 5°C. The primary consideration in selecting a heating rate are potential problems with thermal lag in the sample. Temperature gradients within the sample can broaden transition regions and force them to occur at artificially high temperatures. In contrast, slow heating rates allow the entire sample to equilibrate to temperature change, which, in turn, improves the accuracy of transition temperature assignments.

Applied Force: This only applies to penetration experiments because dilatometric experiments require that the probe be brought into very light contact with the sample. In penetration experiments, applying very low forces may not provide adequate change in the sample to accurately monitor subtle transitions during an experiment; conversely, large forces may actually damage the sample during an experiment. In instruments that use weights, the applied force should be between 5 and 20 g. In servomotor-controlled TMAs, use 0.05 to 0.2 N forces for probe tips with a 0.4-mm radius.

Gas Flows: As with all of the instruments, purge gases provide a stable test environment and ensure uniform heat transfer to the sample. Use the manufacturer's recommended purge rates for all experiments.

TABLE 5—TMA softening point temperatures (°C) and probe displacement values (μm).

Material	Production SPT	Probe Displacement	Rebake SPT	Probe Displacement
Passed	100	1.1	104	0.3
Failed	91	4.8	99	0.9

Special Applications: Many of the newest commercial TMA's are quite versatile instruments and come with special attachments for performing unique experiments. For example, most TMAs come with clamps for tensile testing—good for measuring everything from tensile modulus to shrinkage with age or cure. These techniques almost always require special preparation and operating conditions. Work closely with the supplier when designing these experiments, or, better still, ask the manufacturer for a contact familiar with the technique.

DIELECTRIC ANALYSIS

Dielectric thermal analysis (DEA) is a convenient nondestructive test that relates fundamental molecular motions to a variety of polymeric properties. Applications in coatings science include the characterization of new materials and processes, cure studies, film formation studies, formulations optimization, applications development, performance prediction, competitive product evaluation, and QC/QA applications. General descriptions of dielectric properties can be found in a variety of papers [*27,39–41*].

Because engineering limitations prohibit the characterization of the complete continuum of dielectric properties, there are a number of commercial dielectric analyzers available, each offering advantages in their potential range of applications. The operating principle of all of these instruments, however, is the same: a polymeric system is polarized in an electrical field and the time, temperature, and frequency-dependent dielectric relaxations monitored. Commercially available instruments may be divided into two broad categories: those polarizing samples with an alternating current (ac) and those using a direct current (dc). Each instrument may also have one or more sensors or analytical configurations; these include remote single-surface, ceramic-single-surface or parallel plate geometries.

All dielectric analyzers measure two fundamental electrical characteristics of a material—capacitance and conductance. Capacitance measures a material's ability to store electrical charge, and conductivity measures its ability to transfer electric charge. These components are used to determine geometry-independent values for the material's permittivity (e') and loss factor (e''), serving as molecular probes that correlate with the changing chemical and physical states of the material. Permittivity corresponds to the alignment of dipoles in the electrical field; permittivity values are relatively low at temperatures below Tg or in highly cross-linked polymers and relatively high above the Tg. The loss factor corresponds to the amount of energy required to align dipoles and move ions in the electrical field. The latter term is frequently used in monitoring rheological changes during processing or for monitoring the progress of a cure reaction. More complete descriptions of the use of dielectric analysis in thermal analysis [*9*], film formation [*42*], and thermoset cross-linking [*43–45*] can be found elsewhere.

Thermally stimulated current (TSC) represents a relatively new approach where dipole moments are polarized in a d-c field at temperatures above the sample's main transition temperatures [*46*]. Following polarization, the sample is quench cooled to a low temperature, and then scanned at a constant heating rate through the polarization temperature. As the sample depolarizes, the charge stored in the polarization process is then measured as a function of time. Current peaks obtained this way correlate well with transition temperatures obtained by mechanical relaxation, DSC, or by a-c dielectric spectroscopy.

Another d-c technique—relaxation map analysis (RMA)—is closely allied to TSC and represents a sophisticated extension of TSC experiments. According to theory, this procedure isolates the individual relaxation modes that constitute a typical TSC by varying the polarization temperature and monitoring the depolarization current over small (less than 5°C) temperature "windows." In this way, individual relaxation modes can be isolated from the entire spectrum of modes that make up a typical TSC curve. An Arrhenius plot of the individual relaxation times forms a relaxation map for a material. Coatings characterization using TSC and RMA is described in more detail elsewhere [*47,48*].

Although the dielectric techniques date back to the early 1900s, the lack of high-quality equipment and the attendant experimental difficulties limited the value of DEA for coatings characterization and in materials science generally. Advances in engineering design have dramatically improved the utility of commercial DEAs and rekindled interest in the technique. DEA now promises to play an important role in coatings characterization. The two examples described here—powder coating cure and resin characterization—underscore the value of DEA for coatings characterization. Ceramic single-surface sensors were used in both of the studies.

Powder Coatings—Changes in the complex permittivity e^* of unpigmented powder coatings were correlated with the melt transition (about 60°C) and the onset of cross-linking (about 100°C) in these powders. Dielectric measurements, particularly transition temperatures and relative intensities, correlated very well with DSC results. Five powders, each formulated at different cross-linker levels, were scanned during and after cure. Figure 11 illustrates a typical DEA plot combined with results from the DSC. As the results show, major transitional features in these two sets of data correspond closely. One significant deviation occurs in the region between roughly 65 and 80°C where e^* exhibits a dramatic increase at all frequencies; there is virtually no DSC response over the same temperature range. The increase in e^* probably coincides with increasing molecular mobility as the polymer's volume increases above the melt. Dielectric properties should change rapidly over this temperature range while changes in enthalpy (and therefore DSC heat flow measurements) should be minimal.

Resin Properties—A comparison of the dielectric properties of an appliance powder coating formulated with polyester from two different manufacturers reveals distinct differences. Figure 12 reveals differences in the breadth of the melt transition and the cure onset temperature. Although the performance properties of the resins were indistinguishable, the DEA results clearly indicate the technique's sensitivity to relatively small differences in materials that were virtually identical by all other measures.

Film Formation—The complexity of the film formation process in coatings, particularly latex coalescence, makes this

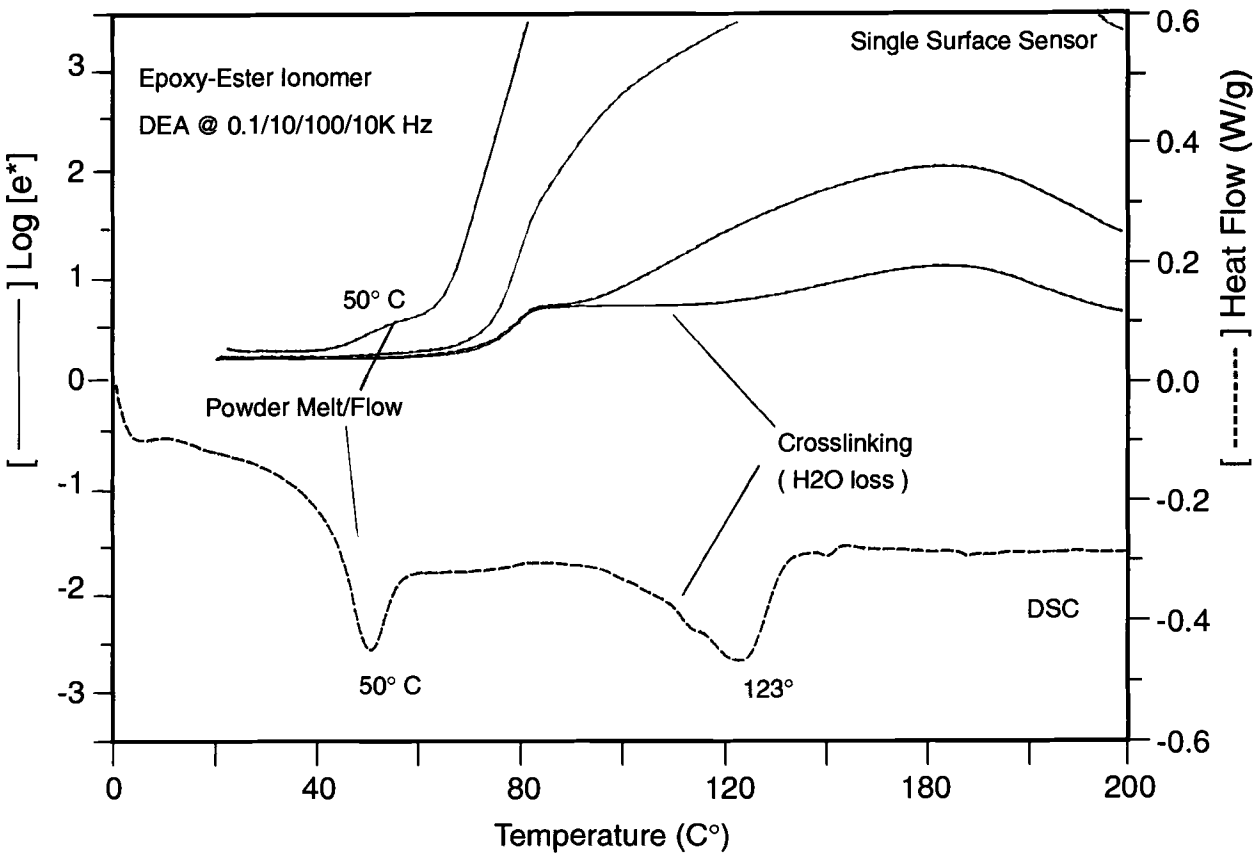


FIG. 11–DEA and DSC results for powder coating cure.

a difficult subject to characterize and understand. Improvements found in newly available dielectric analyzers indicate that DEA will offer, at the very least, a significant step forward in our ability to follow film formation. Figure 13 follows the change in the dielectric constant (complex permittivity) in two latexes, one catalyzed and the other uncatalyzed, after they were applied to a DEA sensor. By comparing the changes in log e^* with the observations from optical microscopy, DSC and TGA (results not included here), some inferences about the nature of the film formation process were made. In the catalyzed sample, the drop in e^* over the first 20 min of the experiment correlates to the loss of free water. Between roughly 20 and 30 min, the latex particles begin to deform and pack tightly together. Finally, over the next hour or so, there is a loss of ionic mobility that probably coincides with polymer interdiffusion at the particle-particle interface. The catalyzed latex had formed a clear, uniform film by the end of the experiment.

The dielectric behavior of the uncatalyzed film was far different. While changes in permittivity associated with water loss and particle packing were evident, the lengthy period thought to correlate with interdiffusion was missing. In fact, this latex was a poor film former, leaving an opaque, severely cracked film on the surface of the sensor.

Coatings Characterization by DEA

Sample Preparation: This depends very much on the type of sensor used. Parallel plate sensors are typically used for free films, while film formation studies would typically employ single-surface sensors. As with other approaches, free films should be made in well-controlled environments and *must* meet the minimum film thickness specifications of the manufacturer. Whenever possible, though, the sample thickness should closely approximate the thickness of the coating after application. As noted earlier, free films can be made by coating low-energy surfaces like PTFE or polypropylene or coating thin aluminum sheet stock and dissolving the aluminum (after the film has formed, of course) with an alkali.

Single surface sensors can be used for any material, but they are especially useful for studying liquids or materials that require a gas/polymer interface for proper analysis. Applying liquids, for example in film formation studies, often requires special preparation to ensure that the electrode surface is completely and evenly covered. For example, when studying low-viscosity liquids, we first calibrate the sensor, then build a low silicone polymer border at the edge of the electrode to keep the sample in place. The volume of liquid applied should leave a final film roughly twice as thick as the distance between electrodes when the sensor uses interdigitated comb electrodes. Always use analytical pipettes to ensure that the applied volume is uniform from experiment to experiment. While absolute measurements of dielectric properties may be in doubt using this approach, it is a valid way to make relative comparisons provided that each material is prepared and handled in *exactly* the same way.

Frequency Selection: In general, there are two components of the dielectric response to an applied electrical field: dipole polarization and free charge migration. The former is most frequently associated with high frequencies (100 kHz or

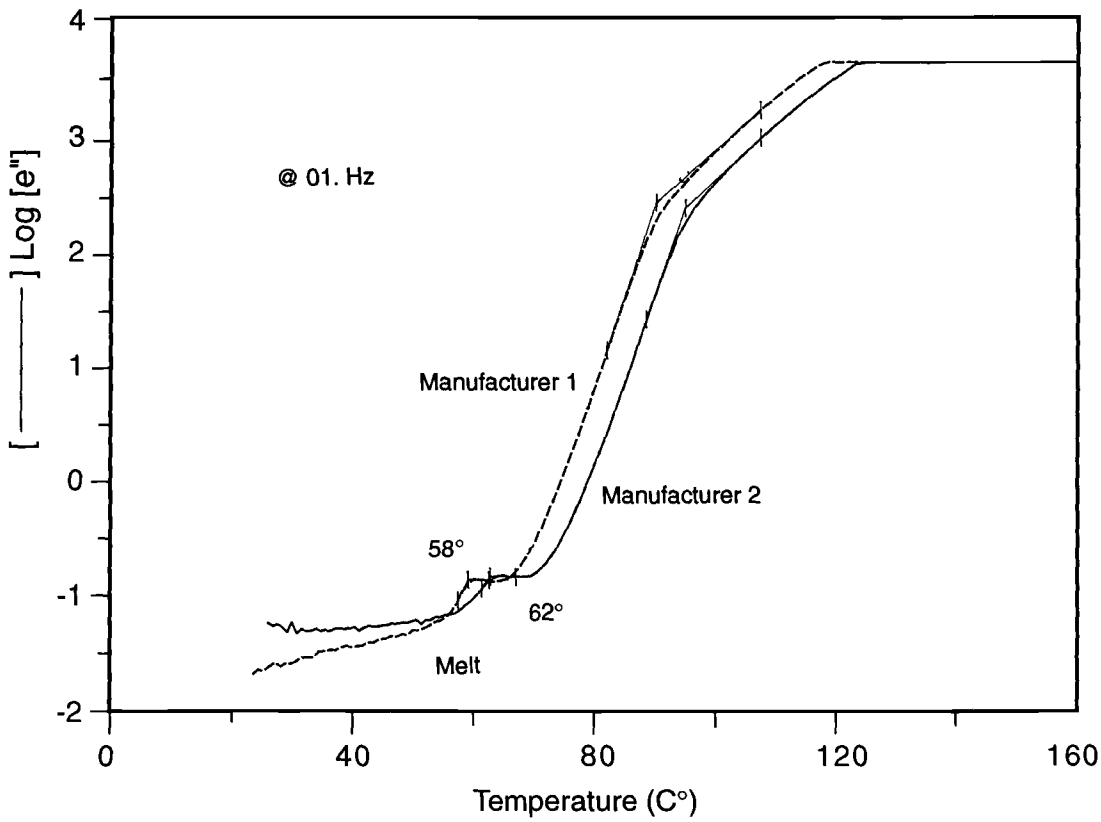


FIG. 12–A comparison of the dielectric properties in identically formulated resins from two manufacturers.

more) while the latter is associated with lower frequencies. Because the dielectric response of polymers varies widely in polymers (and sometimes within classes of polymers), there are no specific rules governing the selection of a test frequency. As a general rule, apply as broad a range of frequencies as your equipment will allow early in the experimental process. After the kinds of responses for given material are better understood, use more limited frequency ranges in subsequent experiments.

Heating Rate: This is an extremely important factor that depends inherently on the frequencies selected for an experiment. Our heating rates are chosen to ensure that we have approximately one data point for each °C increment at each frequency. Low frequencies (<0.1 Hz) require slow heating rates so that the sample has reequilibrated after imposing the a-c electrical field. For example, if we choose to test at frequencies ranging from 0.1 Hz to 100 kHz in order of magnitude increments in our equipment, then a complete cycle (six frequencies) takes about 1.1 min. Based on this cycle time, we would choose a 1°C/min heating rate. Cycle times are much faster at higher frequencies, usually less than 0.2 min, so correspondingly higher heating rates may be used. In isothermal studies we usually collect about 6 to 12 data points per applied frequency for each minute of the experiment depending on the length of the experiment.

Gas Flows: Where possible, apply a uniform gas flow. As with the DMA, we set our gas flow rates so that the oven chamber "turns over" about once every 1 to 2 min. Since the size of the oven chambers in various instruments varies considerably, flow rate requirements will as well. If in doubt, use the manufacturer's recommended purge rates.

Most DEAs are also excellent instruments for running controlled atmosphere experiments. For example, controlled humidity experiments (to 80% RH) require bubbling the purge gas through water (or a salt solution of known humidity) before entering the instrument chamber.

THERMOSET CURE STUDIES

The interrelationship between the network formation process and performance properties make cure process studies critically important in product development. A thermoset coating's performance properties depend inherently on cure conditions. Important characteristics of the cross-linking reaction include the gel point, Tg, and the kinetics of the cross-linking reaction. These properties establish a quantifiable link between the cure reaction and the development of thermoset properties. In essence, they provide a way to "picture" the cure process and a tool for optimizing materials handling, processing, and cure.

Characterizing cure behavior also helps to distinguish between complete cure and optimum cure, an important distinction in thermoset applications. Completely cured thermosets are "ideal systems" where the cross-linking reaction has reached 100% conversion and properties are constant for practical purposes. Optimally cured thermosets are "non-ideal" systems where the cross-linking reaction is incomplete and satisfactory performance properties rather than 100%

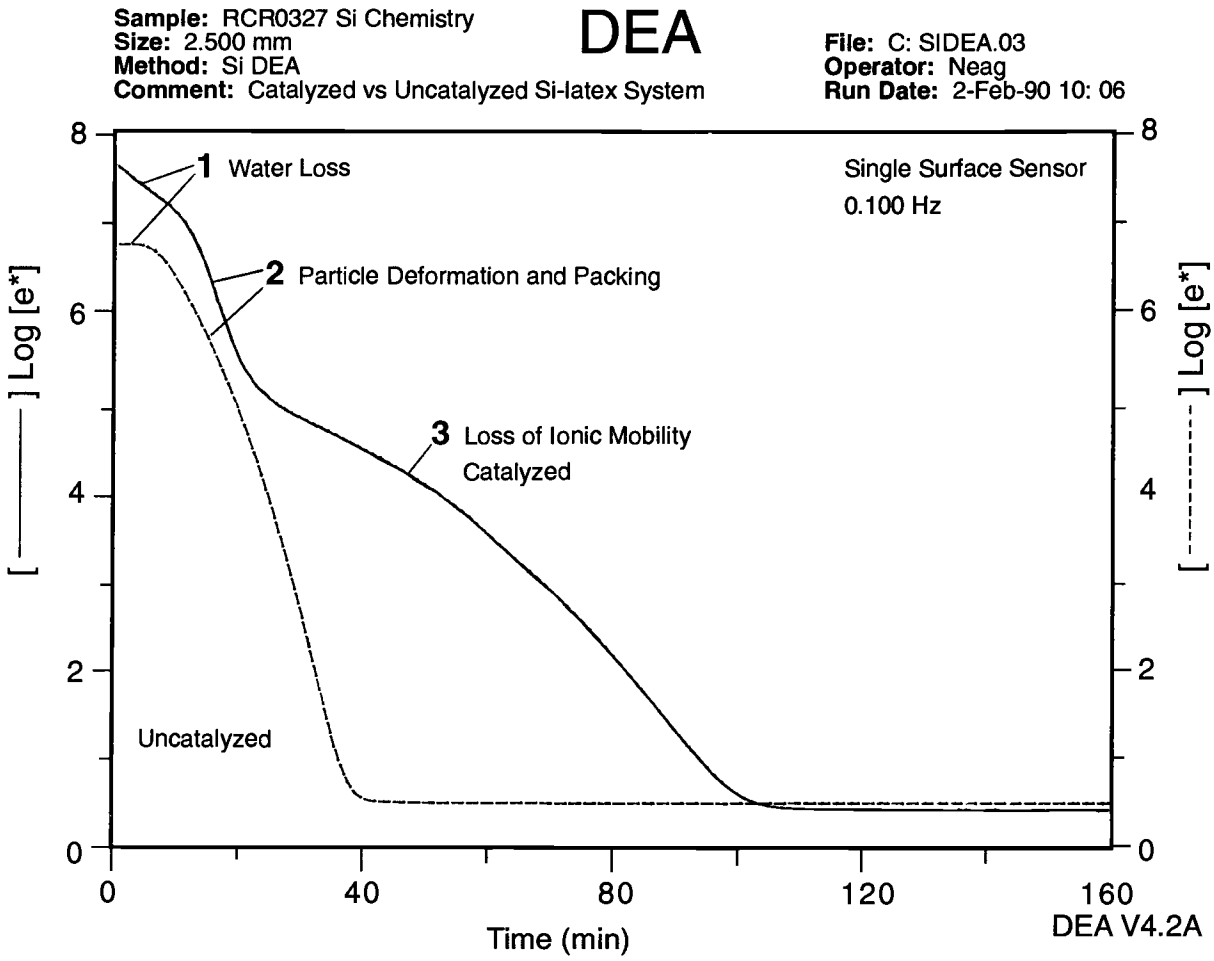


FIG. 13–Changes in complex permittivity during latex film formation.

chemical conversion mark the end of the cure process. In practice, coatings can usually be categorized as nonideal thermosets.

DSC Cure Studies—DSC cure studies have been particularly beneficial in optimizing cure schedules for gel coats—polyester/styrene thermoset coatings used in marine and sanitary applications. The initiation of the cure reaction in gel coats begins with the decomposition of a peroxide and the subsequent copolymerization of styrene with unsaturated groups in the polyester resin backbone [*49*]. When fully cured, these systems are highly cross-linked. Elementary kinetics analysis [*50*] indicates that the reaction order should be 1.5, first order in monomer and half order in initiator.

Evaluation of the kinetics of the gel coat cross-linking reaction using DSC and FT-IR agreed remarkably well. The data in Table 6 also show that the order of reaction obtained by both DSC and FT-IR almost match the value of 1.5 obtained using a theoretical kinetics approach.

TABLE 6—Kinetics parameters for the cure of gel coat resins.

	n	E, kJ/mole	ln A, s^{-1}
DSC	1.56	105.0	28.4
FT-IR	1.54	107.6	29.2

DSC studies revealed that the onset of the gel coat cure process corresponds to the decomposition of the peroxide initiator; according to these results, the reaction began at about 75°C and ended just prior to 150°C. The temperature range (72 to 148°C) selected for the kinetics evaluation using DSC was based on FT-IR spectra. These results showed that the reaction of styrene, and presumably its reaction with the polyester, began and ended at similar temperatures in the DSC and FT-IR. FT-IR reaction kinetics were based on the disappearance of the styrene vinyl group (779 cm^{-1}). While both methods produced excellent results, the DSC results were obtained in a single temperature sweep, while the FT-IR results required significantly more experimental effort to produce and analyze. Results for gel coat cure by DSC, FT-IR, and also DMA are covered in detail elsewhere [*51,52*].

DMA Cure Studies—As a thermoset cures and the number of cross-links increases, a coating's modulus, or resistance to deformation, also increases. In dynamic mechanical analysis, a rise in resonant frequency or relative modulus parallels the development of properties during network formation. The characteristic rise in relative modulus—particularly its rate and intensity—reveals much about the cross-linking process. The curves in Fig. 14 illustrate how a coating's relative modulus (or stiffness) and damping (energy dissipation) change during cross-linking or film coalescence. Throughout the

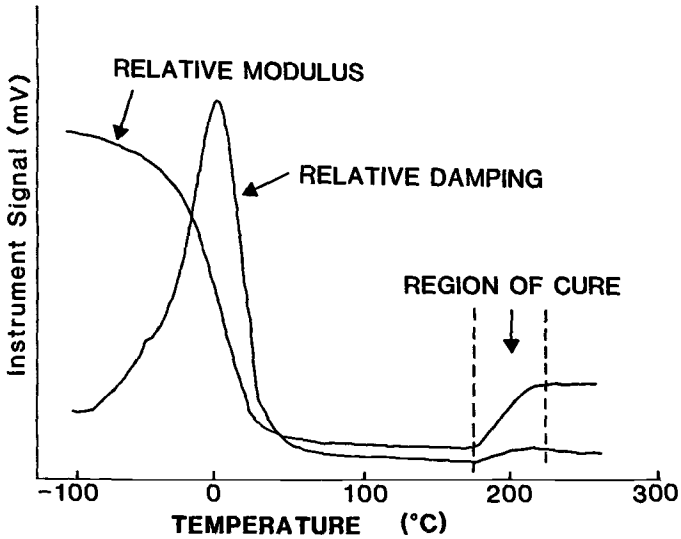


FIG. 14–Generalized dynamic mechanical cure response.

glass transition region—between roughly −80 and 20°C—the relative modulus of the sample decreases until it reaches a minimum. Between 50 and 180°C, the coating is really a low-viscosity liquid that has little measureable dynamic mechanical response. The only measurable mechanical response in this region is due to the substrate used in the experiment. As the temperature increases, cross-linking (or film coalescence) begins and the relative modulus begins to rise. When the reaction is complete, about 220°C in this example, the development of mechanical properties reaches a plateau.

Cure studies by DMA can also help explain the interrelationship between cross-linker characteristics and the cure process. Figure 15 shows the change in the rate and degree of cure in relation to the reactive groups on melamine cross-linkers. As the imino (—NH) concentration increases, the rate and degree of cure both increase. At low imino levels, the rate and degree of cure are low; beyond about 15% —NH, the rate of cure changes significantly, while the DOC appears to reach an asymptotic limit.

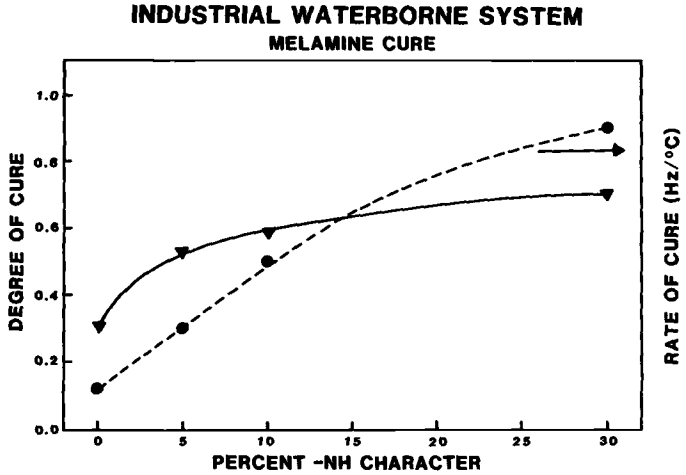


FIG. 15–The relationship effects of cross-linker characteristics on the rate and degree of cure of a waterborne coating.

When the experimental objective is to make a quick comparison of the effects of formulation variables like cross-linker levels or catalyst levels, simple cure curves like these offer an excellent way to make qualitative judgments about the cure process. Sometimes, however, customers may demand more than simple "faster/slower" or "more/less" comparisons. For example, a customer may want to know how long the film formation process will take under a variety of cure conditions different, often substantially different, from those used in past experiments. In cases like these, models of the film formation process are a valuable tool for predicting the time required to complete the film formation process. The virtue of modeling lies in its ability to provide a well of information from a relatively small database or, in this case, a few film formation experiments.

The time-temperature superposition (TTS) approach, while somewhat more demanding experimentally, is a far more versatile method for characterizing the cure process than individual cure scans. This approach uses a series of isothermal cure curves (usually four) to determine the activation energy for the cross-linking process. Once the activation energy is known, an Arrhenius model is used to predict relative rates of cure at different isothermal cure temperatures. The curves shown in Fig. 16 illustrate portions of the storage modulus curves typically used in TTS cure studies. These curves were obtained for an epoxy-polyester powder cured at four isothermal temperatures. The characteristic form of these "cure" curves discloses several important aspects of the cross-linking process, such as the time to gelation, the rapid increase in relative modulus during cure, and a plateau region that marks the end of the cross-linking process.

From a processing perspective, the onset of the rise in modulus about 3 min into the "bake" scan represents the most important feature of the curve. The onset of the rise in frequency in these curves approximates the time to gelation, or the point where the polymer transforms from a viscous liquid to an elastic gel; this point marks the processing limit of the thermoset. Beyond this point, cross-link density increases, approaching a plateau which marks the end of the cross-linking process. In Fig. 16, these powder coatings fail to reach this plateau, even at the highest cure temperatures and/or longest cure times. The continued rise in relative modulus indicates incomplete network formation, even after 100 min at temperatures as high as 210°C. Longer cure times or higher cure temperatures would eventually establish the end-point of the cure process. The modest increase in relative modulus at later cure times may be related to annealing effects or some combination of cure and annealing. Generally, thermosets cured to the plateau will possess less damping, have higher Tg's, and are more brittle than thermosets cured to a point below the plateau.

Degree of cure curves for powder coatings were obtained from DMA data by measuring the increase in relative modulus (measured as a frequency increase here) occurring as cross-linking proceeds. The DMA degree of cure was calculated from Eq 1 below. This equation allows the estimation of the relative degree of cure between the gel point (0% DMA DOC) and the fully cured thermoset (100% DMA DOC). In these experiments, the gel point is defined by the initial rise in the modulus curves. This point in the modulus curve marks the formation of an intractable gel. Full cure is defined by the

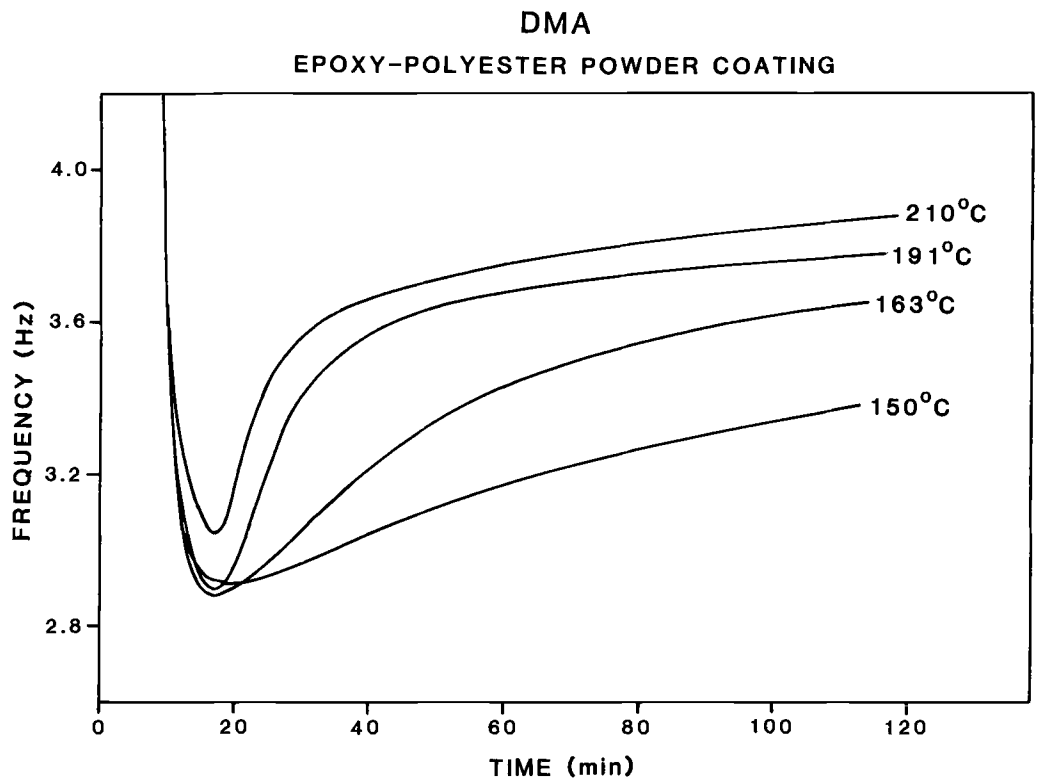


FIG. 16–Dynamic mechanical cure response of an epoxy polyester powder coating at four isothermal temperatures.

plateau region of the modulus curve occurring just after the sharp rise in modulus.

DMA DOC is defined as:

$$\text{DMA DOC} = \frac{\text{Hz}(t,T) - \text{Hz}_{\min}}{\text{Hz}(\infty,T) - \text{Hz}_{\min}} \quad (1)$$

where $\text{Hz}(t,T)$ is the frequency measured during cure at time t and isothermal temperature T; $\text{Hz}_{\min}$ is the minimum pregelation frequency (roughly equivalent to the resonant frequency of uncoated stainless steel mesh) and $\text{Hz}(\infty,T)$ is the frequency of a fully cured coating at temperature T after reaching complete cure.

The DMA degree of cure curves shown in Fig. 17*A* reveals that the rate and degree of "mechanical cure" vary dramatically with the cure temperature. These differences carry important kinetic information about the cure process, information that forms the basis for generating mathematical models of the cure process. By applying a time-temperature superposition method developed by Prime [*53*], the data from the isothermal cure curves at several different isothermal temperatures can be shifted to form DMA degree of cure mastercurves.

Based on the shift factor required to superimpose the data of Fig. 17*A*, the activation energy for the epoxy-polyester cure reaction in this example was estimated at 77.4 kJ/mol. As the DMA mastercurve in Fig. 17*B* shows, the superposition of data to times at 191°C is very good. The key advantage in applying reaction kinetics analysis in dynamic mechanical analysis (and other applicable techniques) is efficiency: a few experiments can provide as much information about the cure behavior as far more extensive laboratory work under many different baking conditions. For example, in Fig. 18, simulated DMA degree of cure curves were generated at three bake temperatures and compared with the DOC at minimum impact resistance. The time required to reach a minimum performance level varies considerably; at 150°C, the coating fails to reach the minimum DOC even after 90 min. At 177 and 204°C, minimum DOC is reached after roughly 15 and 30 min, respectively. Obtaining the same information by a conventional experimental approach would require a considerable amount of time and effort in the laboratory. Moreover, techniques like the DMA TTS methods described here can predict the time required to reach a specified level of performance for any isothermal cure schedule.

COMBINED TECHNIQUES IN PROBLEM SOLVING

Thermal techniques usually reserved for routine analysis and characterization or research support are also useful for solving problems that arise in process or production. Because problems in manufacturing present unusual experimental difficulties, solving them usually requires several methods for adequate characterization. A solitary piece of evidence, whatever the quality, usually needs corroborating information from other sources. Multiple techniques are particularly valuable in settling financial or legal claims where the need for undisputable evidence becomes preeminent. In the example described below [*54*], quality control tests in manufacturing indicated that container coatings sprayed on the interior of aluminum beverage cans were improperly cured, the cus-

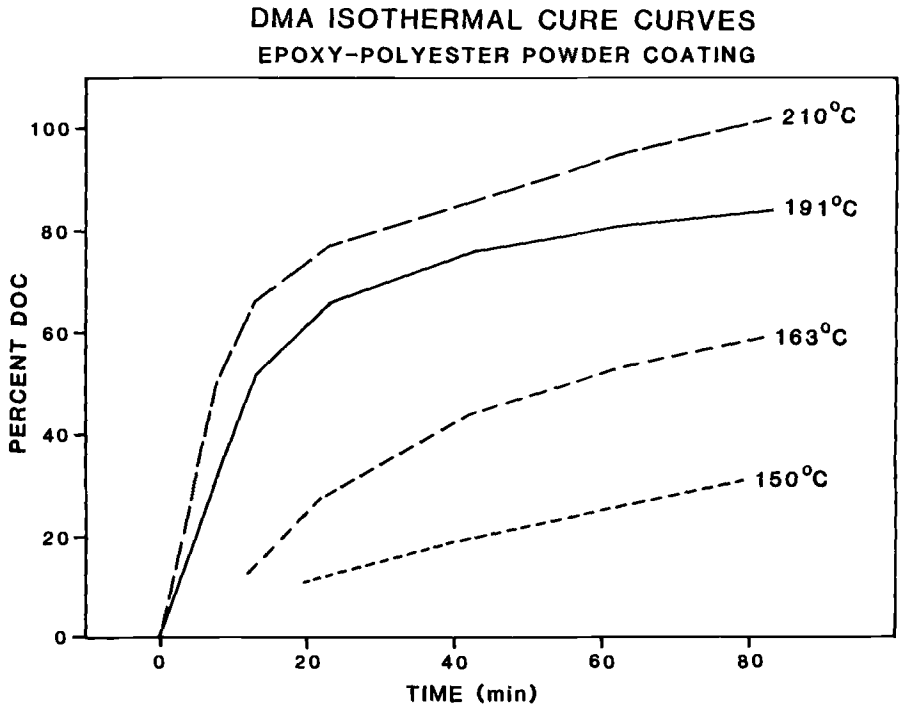


FIG. 17*A*–Epoxy polyester powder coating degree of cure curves.

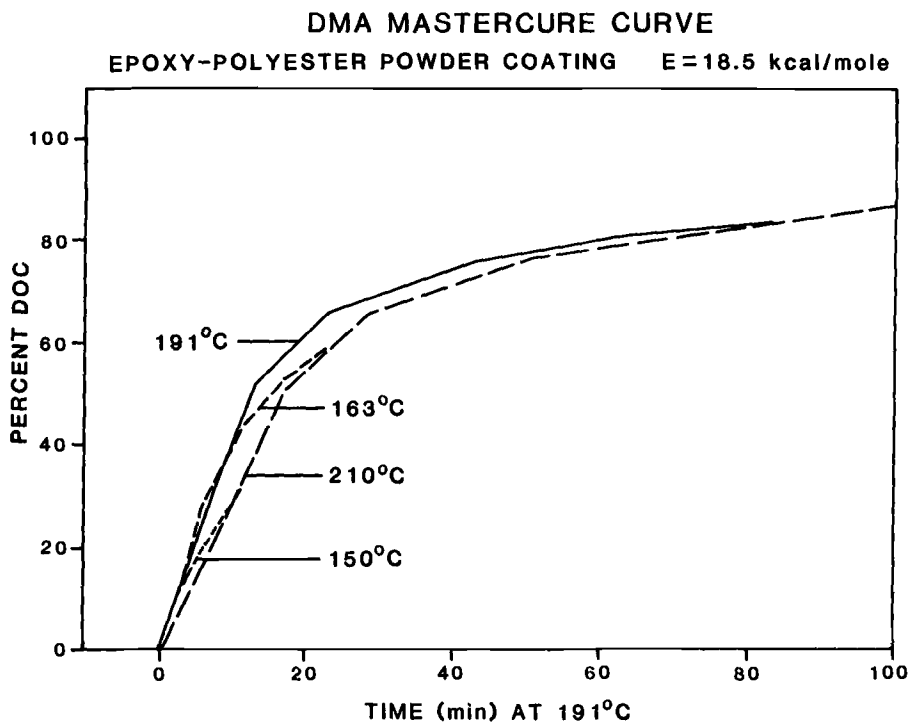


FIG. 17*B*–Epoxy polyester powder coating DMA mastercurves for cure at 191°C and an activation energy of 18.5 kcal/mol.

tomer attributing the cure problem to errors in the synthesis or formulation of the coating.

Four analytical techniques were required to adequately characterize various coating materials and pinpoint the cause of the problem. Compositional differences were assessed by FT-IR; morphological characteristics were observed with scanning electron microscopy (SEM); DSC was used to assess differences in thermal behavior; and relative cure kinetics were measured using DMA. Each of the analyses revealed that differences between the problem coatings and other materials—either laboratory standard or production line standards—were not due to differences inherent in the

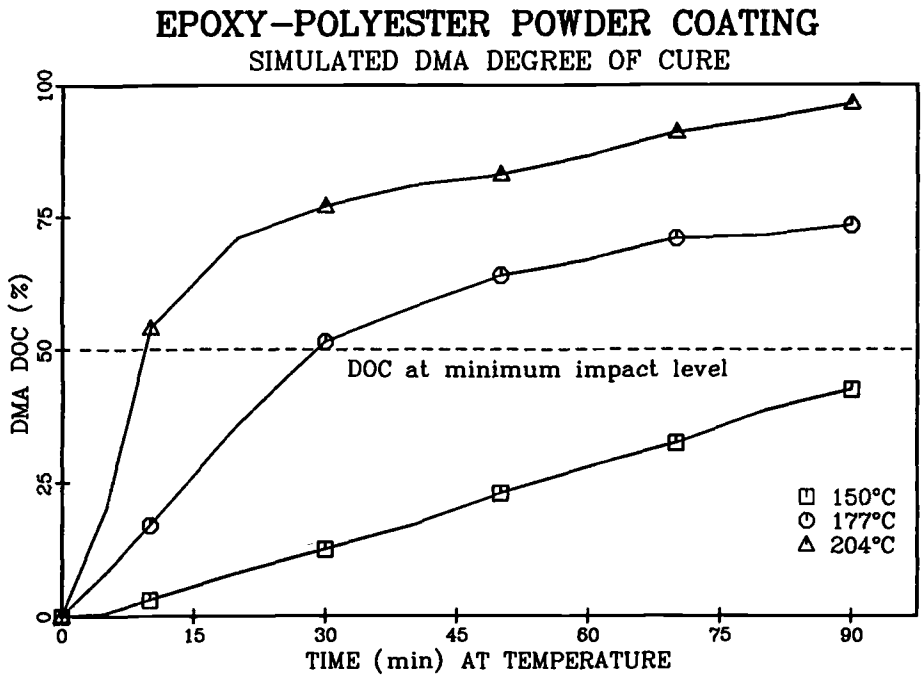


FIG. 18–Predicted time to minimum acceptable impact resistance at three isothermal bake temperatures.

chemistry of the coatings or formulation. Instead, these tests revealed that oven temperatures were probably too low to properly cure the coatings. After raising the oven temperature a few degrees, all of the coatings passed the QC test. Figure 19 compares the DSC heat flow characteristics of a properly cured standard with curves of the problem coating before and after rebake. The key feature shown in this figure is a weak endotherm, apparently related to the level of cure in the problem coating. After rebake, this endotherm disappears and the thermal behavior of the problem coating is virtually

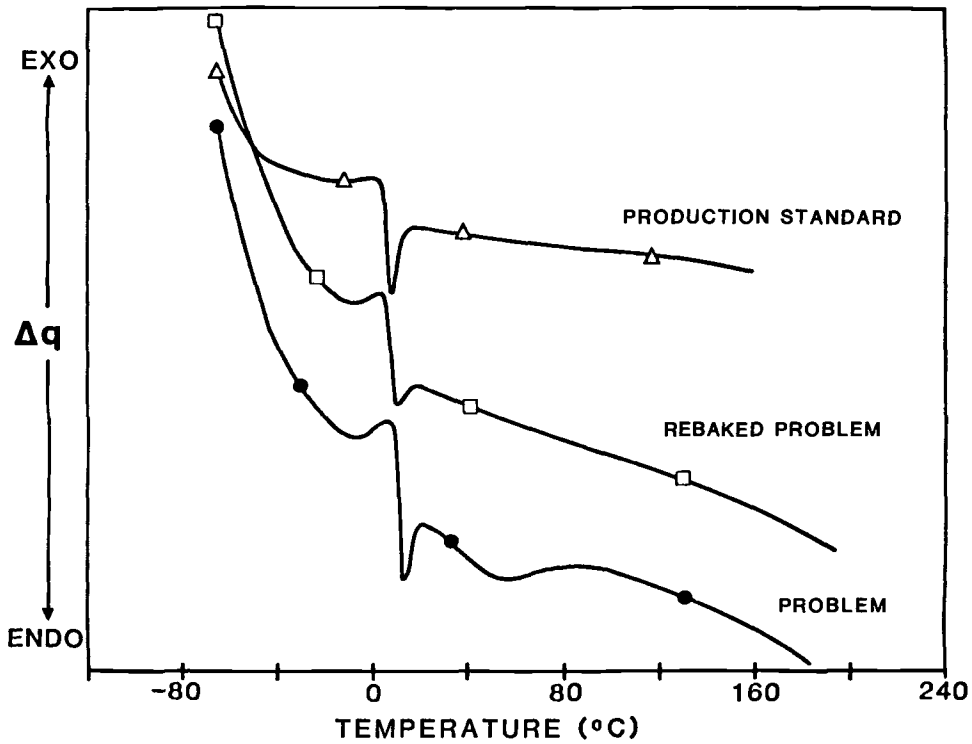


FIG. 19–Comparison of the DSC heat flow characteristics of a production standard, a problem coating, and the rebaked problem coating (Δq = heat flow).

identical with that of the properly cured coating. Similar comparisons using FT-IR to follow changes in reactive sites during cure showed that the "good" and "bad" coatings were virtually indistinguishable (provided that their thermal histories were the same). In fact, the results obtained from each of the instruments led to the same conclusion: when the problem coating was rebaked, it was virtually identical to the properly cured material. Taken together then, these results showed that the manufacturing problem was unrelated to the coating's chemistry. Instead, QC failures were caused by oven temperatures set too low to properly cure the coating.

SUMMARY

Thermal analysis occupies a unique place in research and development. In most instances, the utility of an analytical technique is strictly limited by its output. For example, spectroscopic tools like NMR or IR tend to be viewed as standalone operations that provide a specified result. TA differs from other analytical operations because the instruments offer greater versatility. In fact, thermal analysis is generally recognized as a broad technology encompassing many instruments and many more applications. Depending on the need, the results delivered by TA can range from the straightforward, like Tg's, to the complex, like reaction kinetics parameters.

TA realizes its greatest value, however, when more than one instrument is focused on a research or production problem. In combination, these instruments can provide tremendous insight into the relationship between formulation, processing, and the ultimate performance of material, often clarifying hard-to-understand relationships [*55*]. When applied throughout the product development cycle, these instruments can reduce product development time, manufacturing costs, and, in the end, help shape the best possible product.

Acknowledgment

Thanks are due to the many coworkers at Glidden for their contributions to the work described in this paper. The author is particularly indebted to Leo Tischer, Tony Parker, Mary Logue, Tammy Chalmers, Sharon Chang, and Patti Wilson for their diligence in obtaining much of the experimental data described here and also to Richard Holsworth for his thoughtful contributions to experimental design and the analysis of the results over many years. In addition, Mark Koehler, Ted Provder, Ted Niemann, and Ann Kah deserve recognition for their pioneering efforts in the automation of the DSC and DMA. Without the time savings acquired in data acquisition and analysis made possible through their efforts, much of this work would have been a practical impossibility. Thanks also to Ann for redrawing many of the figures used in support of the text. Finally, I'm indebted to Dr. Stephen Cheng (University of Akron), Dr. Richard Chartoff (University of Dayton), Dr. David Kranbuehl (William & Mary), Dr. Don Burlett (Goodyear), Dr. Charles Earnest (Berry College), and Dr. Peter Kamarchik (PPG Industries) for their valuable comments and insights on instrument operation and experimental detail.

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Ultraviolet/Visible Spectroscopy

by George D. Mills[1]

THE USE OF ELECTROMAGNETIC RADIATION (EMR) for the analysis of paints and coatings is best addressed by looking at the way this energy source is absorbed by the system under investigation. Most EMR analytical techniques attempt to measure the energy difference between the incident beam and the emerging beam and to relate this energy difference at a particular wavelength (energy) to the absorbing species' concentration or chemical makeup. The emerging beam may pass through the system or be reflected from a surface. There are many sophisticated instruments that use EMR, and they operate from the lowest energy bands in microwaves to the highest energy γ-rays. The region of the spectrum most commonly used in the paint laboratory lies between the infrared and ultraviolet bands. The instrumentation operative in this region can be relatively low in price, and the information that can be obtained about concentration and molecular structure is very useful.

Absorption in the infrared region of the spectrum occurs because the atoms within a molecule or ion can react to these specific energies by increasing the amplitude of some vibrational mode. This mode of energy absorption occurs because of the ability of connected atoms to stretch, bend, or move about relative to one another. The energy that can be absorbed in a particular situation is dependent on such factors as strength of the bond, mass of the atoms, interaction of adjacent species such as the remainder of the molecule or solvents, as well as other factors. The energy of EMR in the ultraviolet and visible (UV/VIS) regions of the spectrum is somewhat higher. Because this higher energy affects the electrons within the molecular and atomic orbitals rather than the mass of the atoms, this mode of energy absorption reveals information about the bonding within the molecule or is specific to a given specie. This allows both qualitative and quantitative determinations of species that have the ability to absorb at these specific energy levels.

An important quality of paints and coatings is their visual appearance. Although the visual region of the spectrum is rather small, it is very important when analyzing coating systems. Color and color stability is a very important aspect of paints. UV/VIS spectroscopy can also provide information on concentration of active species, wavelengths of highest absorption, filtering efficiency of UV protection additives and their optimal concentration, as well as other needs. Transmission spectroscopy is useful in performing analysis on solutions containing binders, stabilizing additives, and coloring agents such as dyes. UV/VIS reflectance and fluorescence spectroscopy provides information about color and general appearance.

Polymerization of some very fast curing systems use UV as the initiating energy source. These curing mechanisms employ free radical and cationic initiation and propagation for film formation, and they are often the preferred coating materials for very fast moving, highly productive coating lines.

Binders, additives, and pigments that absorb at frequencies in the ultraviolet and visible region may suffer degradation from these energetic absorptions. While the techniques used for UV/VIS spectroscopy may be helpful in determining the frequencies at maximum degradation and may assist in engineering the optimum stability package for the coating system [*1*], degradation testing per se is addressed elsewhere. UV exposure testing and weathering analysis employ test procedures such as ASTM Practice for Conducting Tests on Paint and Related Coatings and Materials Using Filtered Open-Flame Carbon-Arc Light and Water Exposure Apparatus (D 822), ASTM Practice for Testing Paints, Varnishes, Laquers, and Related Products Using Enclosed Carbon-Arc Light and Water Exposure Apparatus (D 5031), ASTM Practice for Conducting Tests on Paint and Related Coatings and Materials Using a Fluorescent UV-Condensation Light and Water-Exposure Apparatus (D 4587), and other standards currently under revision.

The objective of this chapter is to discuss the use of UV/VIS spectroscopy in the analysis of coating systems and components. It is important to be mindful of the actual mechanism of absorption. This is closely tied to molecular structure and will allow a better understanding of the total task of engineering the coating formulation with maximum life expectancy for the end use environment as well as allowing the design of quality control techniques useful at the manufacturing level. At the values of energy levels represented by the frequencies of UV radiation, certain chemical bond energies can be surpassed. A knowledge of the mechanism of UV absorption can be helpful in allowing better choices for binders that may be susceptible to degradation, development of UV-initiated polymerization catalysts [*2*], as well as allowing judicial choices of UV stabilizers for those coating systems.

It is important that the paint analyst be aware of the principles of operation of the instrumentation used to probe paint systems and components. This will allow for a clear understanding of what the information received really means. It is also very important for the analyst to know the limitations of his instrumentation. Action taken on poor data can be far worse than taking no action taken at all!

[1]President, George Mills & Associates International, Inc., P.O. Box 847, Humble, TX 77347-0847.

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ELECTROMAGNETIC RADIATION

Electromagnetic radiation is a form of energy that possesses both wave-like characteristics and particle-like characteristics. The wave-like nature allows the radiation to travel at extremely fast velocities and to be refracted. Unlike sound, this energy form may be transmitted through the vacuum of space without a supporting medium. As a particle, when radiation interacts with matter, it is absorbed in discrete packets of energy called photons. The radiation is composed of an electrical field of oscillating field strength superimposed on an oscillating magnetic field at right angles to one another.

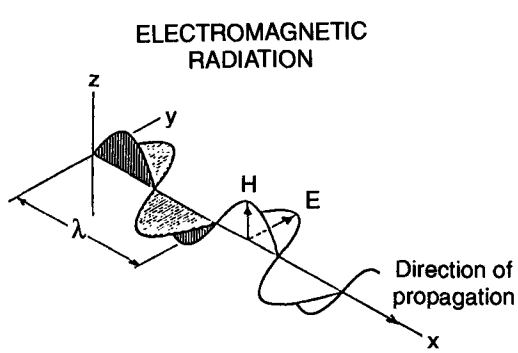
If the vectorial values for the electrical and magnetic field strength are plotted as a function of distance from the moving point charge that is generating the EMR, the graphical presentation in Fig. 1 is obtained. In this plot, the magnetic field strength, $\vec{\mathbf{H}}$, is represented as a vector in the *xz* plane, and the overlapping plot of the electric field strength, $\vec{\mathbf{E}}$, is presented as a vector in the *xy* plane. The direction of propagation is down the *x* axis. This represents the plot of a plane polarized wave. If all waves coming from a collection of similar radiators are in the same spacial orientation, we call the radiation *plane polarized light*. In nature, radiation coming from a collection of point sources will usually be randomly oriented and therefore will not be polarized. It is useful to note that when a beam of polarized light passes through a collection of absorbing species that has at least one area of asymmetry, polarized light will be rotated to some degree. This principle is used to obtain information about the shapes of particular molecules and quickly gather information on their concentration.

The wavelength, λ, is usually expressed in units of centimeters, microns, millimicrons, or angstroms. The frequency of the oscillations, ν, is the number of cycles that occur in 1 s and is therefore equal to the speed of the radiation divided by the wavelength.

$$\nu = c/\lambda \tag{1}$$

The reciprocal of the wavelength is called the wave number, $\bar{\nu}$, and is frequently used in spectroscopy. Its units are in reciprocal centimeters. The wave number of the radiation, like its frequency, is proportional to the energy of the radiation, i.e., the higher the wave number the higher the energy of the radiation.

$$\bar{\nu} = 1/\lambda \tag{2}$$



Electric and magnetic field strengths in electromagnetic radiation.

FIG. 1–Plot of the magnetic and electric field strength as a function of distance of propagation away from the generating point charge.

Figure 2 presents the EMR spectrum and the common name usually used for that portion of the spectrum.

It is interesting and useful to understand how this form of energy interacts with the components of coatings. Note that the value of the energy in the UV/VIS band of the spectrum is relatively high, sufficiently so to cause electron excitation in atoms and molecules. When the energy is great enough to cause the homolytic split of the two electrons that form a chemical bond in a molecule, two free radicals are formed. This is quite probable when one (or both) fragments have a degree of stability in the degraded condition. This is the reason for the chalking so common in epoxies. Some crystals are susceptible to degradation as well. The anatase form of titanium dioxide is a good example of UV degradation of crystalline pigments.

Should the system be prone to damage from UV radiation, it is certain that the system will absorb in this region. The testing of coatings for degradation caused by these wavelengths is treated elsewhere, but UV/VIS analysis may assist in determining failure mechanisms, optimum UV screening agent concentrations, measurement of residual stabilizers after testing, and others. Current technology provides UV/VIS instrumentation for use in various modes, similar to that used in the infrared region. This includes transmission mode, fluorescence mode, and specular and diffuse reflectance modes.

BASIC INSTRUMENTATION

The basic optical path or layout of modern scanning instruments has not changed appreciably over the past decade or two. The optical diagram of a modern instrument is presented in Fig. 3. Low-cost computers for doing sophisticated calculations and better diffraction gratings have allowed important enhancements. Increased electronic noise suppression has allowed lower cost-to-benefit ratios in the newer instruments. Software now provides full instrument control, enhanced data analysis including rapid graphics, and considerable options in report generation. Three-dimensional plotting enables easy representation of reaction mixtures, allowing kinetics studies of active systems. While following the

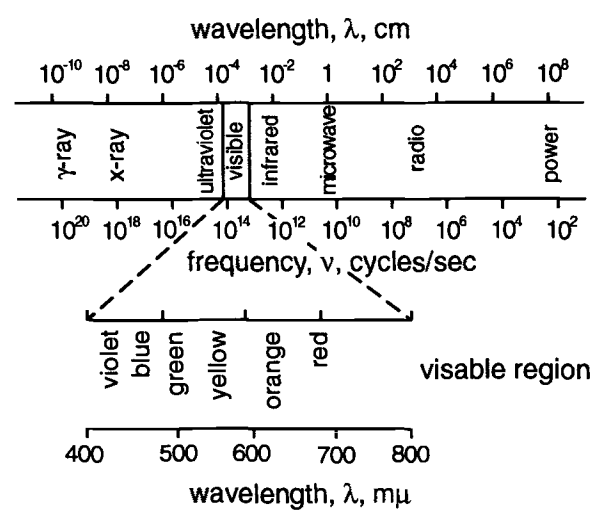


FIG. 2–The complete electromagnetic spectrum.

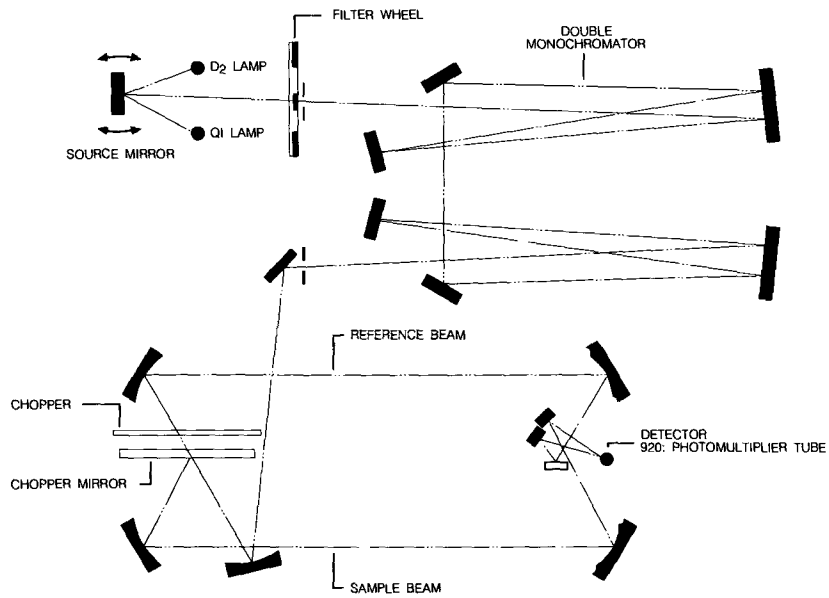


FIG. 3–The optical path of a modern UV/VIS spectrophotometer (Model 920, GBC Scientific Equipment, Arlington Heights, IL 60004).

curing kinetics, it is possible to see the influences of catalysis as a function of temperature.

Principle of Operation

Basically, the classical instrument will have a source of radiation, a method for isolating a very small band of that radiation that is passed through the sample (the "monochromator" section), a sample holder arranged in such a manner as to allow passage of radiation having a low band width, a detector to monitor the quantity of radiation passing through the sample, and a read-out or data collection system. This is represented schematically in Fig. 4.

With the advent of the diode array detector, multifrequencies may now be detected at one time. The schematic for this type of instrument is presented in Fig. 5. Here the sample is irradiated with a broad band of radiation. The light that emerges is then sent to a "monochromatic" device that spreads the radiation out across an array of CCD detectors banked in such a way as to "see" all of the emerging broad-band radiation. The separation of the signal occurs because each area on the detector is read independently and the position where the radiation falls on the detector is a function of its wavelength (energy) for that region of the spectrum. Those parameters that are most important for UV/VIS/NIR spectroscopy include reproducibility, sensitivity, and wavelength range.

Calibration of Instruments

The calibration of instruments having absorptions in the UV/VIS/NIR wavelengths may follow ASTM Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers (E 275) [3]. Here, a mercury arc provides twelve very unique peaks having extremely precise wavelengths for comparison with the values reported by the instrument. Figure 6 presents the mercury arc emission spectrum in the UV/VIS region showing the reference wavelengths.

Another useful standard that provides established specific reference peaks is holmium glass (Corning No. 3130). This standard has the advantage over the mercury arc in that it may be conveniently placed within the instrument with minimum problems. That spectrum is presented as Fig. 7.

SPECTRAL INTERPRETATION: QUALITATIVE AND QUANTITATIVE INTERPRETATION OF SPECTRA

The output of the UV/VIS spectroscopy instrument will usually be a plot of absorbance versus wavelength and is called the absorption spectrum. Absorption of the UV/VIS radiation usually occurs when an electron within the active specie absorbs the energy of a photon. The molecular conse-

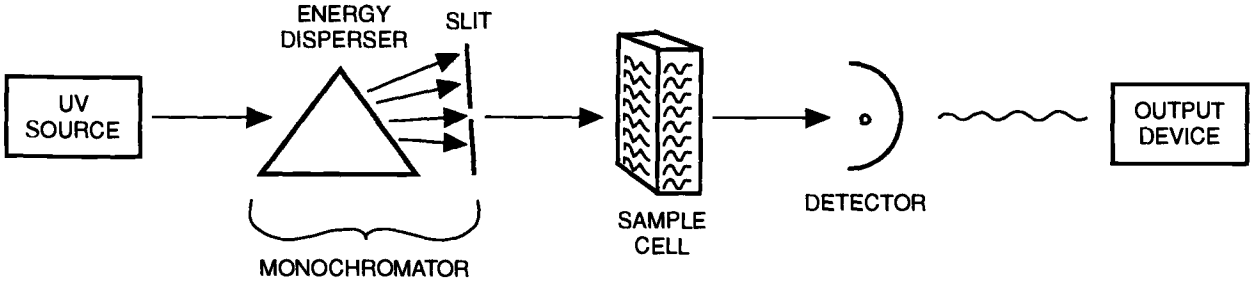


FIG. 4–Component arrangement of the classical UV/VIS instrument.

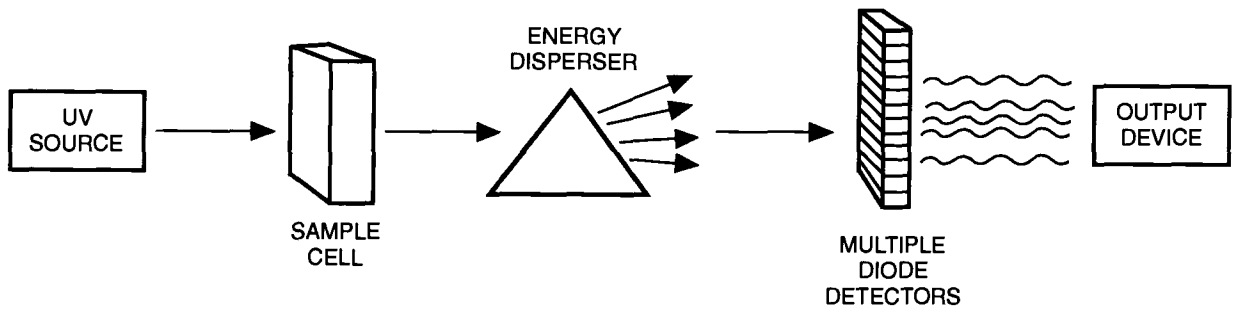


FIG. 5–Component arrangement of the modern UV/VIS instrument using a diode array detector.

quence of the energy absorption process is for an electron to jump to a higher energy level within the specie. This loss of energy in the incident beam is taken as the absorption, and the plot records these losses as a function of wavelength. In most instances, the energetic electron will return to its former stable state by liberating heat. In some instances, the very energetic electron may step down by way of other orbitals. The energy released may then be in the form of radiation, but at a different wavelength. This is the basis of fluorescence spectroscopy and adds another dimension to analysis of some coating components.

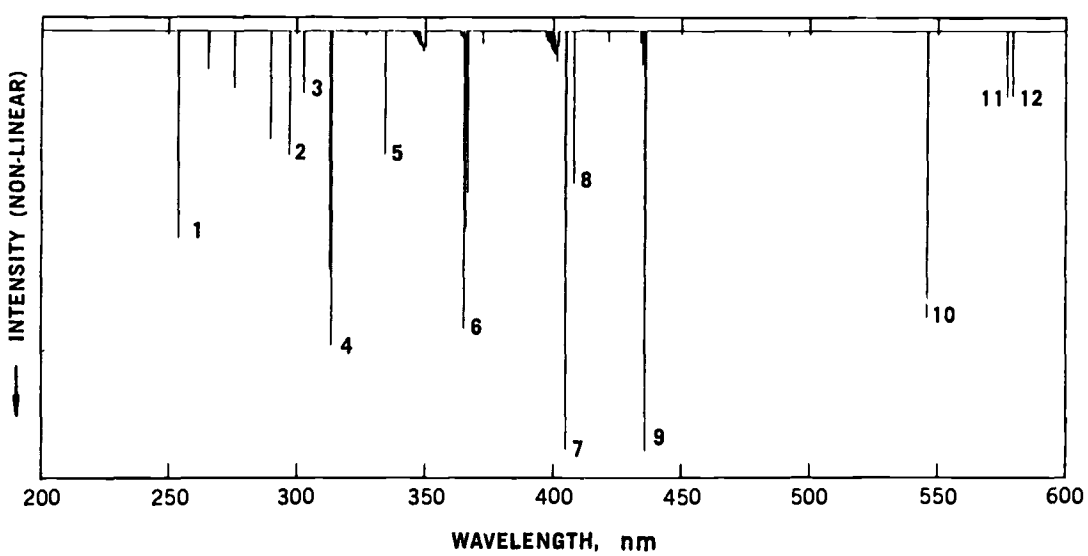
The use of UV/VIS spectroscopy techniques to identify an unknown is possible because the intensity of the absorption at a given frequency is characteristic of the species. By comparing the wavelength at maximum absorption, the intensity tables will provide probable candidates. One such set of tables, about 80 pages, is given in Ref *4*.

The derivation of the quantitative relationship using absorption of radiation requires consideration of the term *radiant power*. Radiant power, P, is the amount of radiant energy striking a unit area per unit time. If we use a constant cell length, two factors affect the amount of power observed at each successive location along the path of a monochromatic incident beam as it passes through the solution. One is the amount of power, P, at the start of each successive arbitrary step along the way, and the other is the number of absorbing species in the path of the radiation. This can be stated as a proportionality. The incremental change in power, ΔP, is proportional to the power of the radiation and the number of absorbing species, ΔN. This may be expressed mathematically as

$$\Delta P = -kP\Delta N \tag{3}$$

The negative is the result of power being lost. By making the intervals between measurements infinitely small, the mathematics reduces to the differential equation

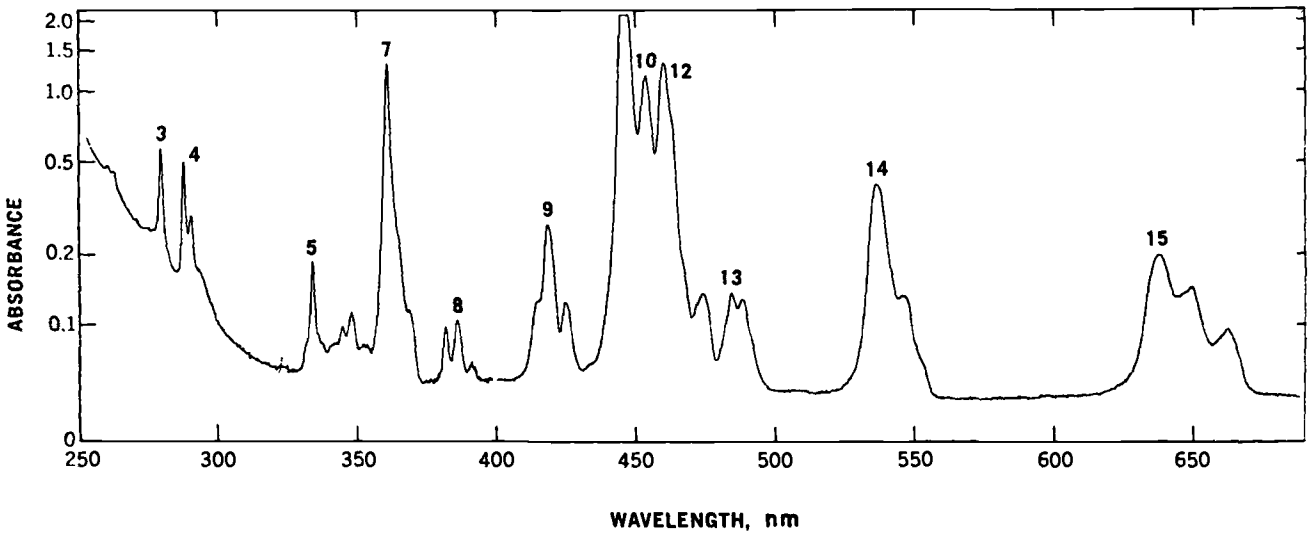
$$dP/P = -k\,dN \tag{4}$$



Line Number	Wavelength, nm	Line Number	Wavelength, nm	Line Number	Wavelength, nm	Line Number	Wavelength, nm
1	253.65	4	313.16	7	404.66	10	546.07
2	296.73	5	334.15	8	407.78	11	576.96
3	302.15	6	365.01	9	435.84	12	579.07

Instrument: Cary Model 14
Scanning Speed: 2.5 A/s
Slit Width: 0.03 mm
Spectral Slit Width: 0.10 to 0.15 nm

FIG. 6–The mercury arc emission spectrum in the UV/VIS region with the corresponding reference wavelengths (from ASTM E 275).



Band Number	Wavelength, nm	Band Number	Wavelength, nm	Band Number	Wavelength, nm	Band Number	Wavelength, nm
3	279.4	7	360.9	10	453.2	14	536.2
4	287.5	8	385.9	12	460.0	15	637.5
5	333.7	9	418.7	13	484.5		

Instrument: Cary Model 14
Scanning Speed: 10A/s
Slit Width: 0.025 to 0.105 mm
Spectral Slit Width: 0.10 to 0.40 nm
Sample Thickness: 2.6 mm

FIG. 7–Spectrum of holmium glass (Corning No. 3130) showing reference wavelengths (from ASTM E 275).

If we integrate between the limits of P_0 when $N = 0$ and P at some value of N, we have

$$\int_{P_0}^{P} \frac{dP}{P} = -k \int_{0}^{N} dN \tag{5}$$

$$\ln (P/P_0) = -kN \tag{6}$$

To convert the actual number of absorbing species to a more convenient term of concentration, c, we consider the volume where contained and Avogadro's number. Thus

$$N = (6.023 \times 10^{23} cbs/1000) \tag{7}$$

where c is concentration in moles per liter, b is the path length in centimeters, and s is the cross-sectional area in square centimeters. When the constants are combined, this yields

$$\log (P/P_0) = \epsilon\, bc = A \text{ (the absorbance)} \tag{8}$$

which is Beer's law.

Beer's law is the basis of all quantitative spectral measurements. This law, often referred to as the Bourger-Beer or Lambert-Beer absorption law, may be stated exponentially, with intensity of the radiation rather than power, as $I = I_0\, e^{-abc}$. The logarithmic form is used more often

$$A = \log_{10} (I_0/I) = \log_{10}(I/T) = abc = \epsilon bc \tag{9}$$

where

A = absorbance (often referred to as optical density),
a = ϵ = molar absorptivity or absorbency,
b = cell path length, cm,
c = concentration, moles/litre,
I_0 = intensity of incident radiation of the sample,
I = intensity of radiation transmitted by the sample, and
T = (I/I_0) fraction of radiation transmitted by the sample or transmittance.

ASTM Practices for General Technique of Ultraviolet-Visible Quantitative Analysis (E 169) is given in Ref 3.

The reliability and sensitivity of the quantitative method will depend on the choice of a suitable band and suitable solvent. The strongest band free of interference from other sample components is usually chosen, but modern computer treatment of data will frequently allow deconvolution of overlapping spectra.

In general, UV quantitative measurements require calibration in the solvent chosen for the method. A simple calibration curve of concentration versus absorbance can be prepared from the standards. However, it is advisable to study all known components to determine interferences.

POTENTIAL PROBLEMS

When the spectroscopist is performing quantitative determinations that require a linear calibration curve, Beer's law must be applicable over the concentrations under investigation. When deviations exist in Beer's law at the concentrations under investigation, extrapolation from one concentration may not be truly representative of the system concentration. Concentration of some active species such as the

high nucleophilic amino functional aromatics used as epoxy cold-temperature catalysts may react with the surface of metal pigments, effectively removing them from the solution and yielding low results.

Another potential problem occurs because Beer's law is based on monochromatic light. The typical band pass of analytical instruments will depend on the technique being used to produce the monochromatic light. The use of prisms and slits can lead to an appreciably high band pass on the order of 10 to 20 nm. Instruments with holographic gratings and automatic peaking can be as low as 2 nm.

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X-Ray Analysis

by A. Monroe Snider, Jr.[1]

X-RAY DIFFRACTION (XRD) and X-ray fluorescence spectrometry (XRFS) are powerful, well-established tools used by analytical chemists in many areas of technology. They have great utility in the coatings industry. In areas where they are applicable, they are frequently the quickest and easiest technique available. XRD is convenient for the identification of diverse crystalline solids encountered in paint research laboratories and production plants. It is particularly well suited for use in the identification and quantitative analysis of crystalline pigments and extenders, either when they are alone or present in paste or paint. XRFS is useful as a stand-alone technique for elemental analysis and as a complementary tool for use with other analytical techniques. X-ray spectrometers typically can analyze all elements with an atomic number of about 11 (sodium) and higher, but some units can reach as low as atomic number 5 (boron). XRFS can span the concentration range from parts per million to high percentages for most elements in liquid or solid samples. Dedicated XRFS units, much lower in cost than scanning spectrometers, can be set up to detect and quantify one or a few specific elements. Portable XRFS units are available for field investigations. The present section summarizes the principles and methodology of XRD and XRFS.

RADIATION SAFETY

Although operation of modern X-ray instruments involves little risk to the operator when proper safety practice is followed, it is imperative that the operator know and follow proper practice. Exposure to excessive quantities of X-radiation is injurious to health. Therefore, users should avoid exposing any part of their bodies, not only to the direct beam, but also to secondary or scattered radiation that occurs when an X-ray beam strikes or passes through any matter. It is strongly recommended that users check the degree of exposure by film badge or dosimeter carried on them. X-ray instruments should not be operated with safety interlocks, shielding, or other protective devices removed or deactivated. Before using the equipment, all persons designated or authorized to operate X-ray instrumentation or supervise its operation should have a full understanding of its nature and should also become familiar with established safe exposure factors by careful study of the American National Standards Institute Standard N43.2-1988, "Radiation Safety for X-ray Diffraction and Fluorescence Analysis Equipment" [*1*]. Inquiries should be made of state agencies about existing requirements.

X-RAY DIFFRACTION

Application

Types of Samples

X-ray diffraction is widely used for the analysis of analytes that are crystalline or polycrystalline solids, i.e., solids comprised of atoms or ions arranged in a three-dimensional lattice pattern [*2*]. The sample may be totally crystalline or may contain one or more crystalline components interspersed with noncrystalline material. Common types of materials analyzed include pigments and extenders (alone, in grind pastes, in liquid paints, or in dried paint chips), miscellaneous crystalline solids, and pretreatment on metal. X-ray diffraction also has important uses in the study of amorphous materials such as polymers and inorganic glasses [*2*]. In the case of scanning X-ray diffractometers, a flat surface of the specimen must be presented to the X-ray beam.

Types of Information Provided

X-ray diffraction analysis permits qualitative and quantitative analysis of crystalline components. It can indicate the degree of crystallinity, crystallite orientation, and long-range order in polymers. Long-range order in liquids has also been studied [*2*].

Range of Concentrations

As a rule, crystalline components can be analyzed by routine methods at concentrations ranging from 100% down to approximately 1 or 2%. However, the limit of detection varies widely with the identity of the analyte of interest, the number and identity of other components, the quality of the instrumentation used for analysis, and the instrument operating conditions. Analysis of components at concentrations as low as 0.01% has been reported [*3*].

Physical Principles

X-ray diffraction experiments are performed by irradiating a specimen of crystalline or polycrystalline material with a beam of X-rays of known wavelength and determining the angle 2θ between the incident beam and each diffracted beam of X-rays and measuring the intensity of each diffracted

[1]Senior research associate, PPG Industries, Inc., Research & Development Center, P.O. Box 11472, Harmarville, PA 15238.

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beam. Diffraction occurs only at discrete angles defined by the Bragg equation [2,4,5].

$$n\lambda = 2d \sin \theta$$

where

n = a positive integer (usually one),
λ = the wavelength of the X-rays used,
d = the distance between layers of atoms of a set of lattice planes, and
θ = the angle between the incident X-ray beam and the lattice plane [5].

The wavelength of the X-rays is determined by the choice of the X-ray tube target material, usually copper, and is thus known. The wavelength of copper K_α radiation, the principal component of X-rays from a copper target, is 1.541 78 Å. It is common practice to use a crystal monochromator or absorption filter to prevent unwanted wavelengths of X-rays from contributing to the diffraction pattern. Angle θ is half of the diffraction angle 2θ that is determined experimentally. The distance between layers of atoms in a set can be calculated by using the Bragg equation. The distance, d, is determined by the diameter of atoms comprising the crystal, the three-dimensional arrangement of the atoms in the crystal, and the set of lattice planes in the crystal that produced the "reflection" of X-rays. Thus, crystallites of different compounds or different crystal modifications of a single compound will give different sets of d-spacings. Each crystalline phase will produce a unique X-ray diffraction pattern that can be used as a "fingerprint" for identification. Detailed discussions of the Bragg equation and the physical basis of X-ray diffraction are available in various treatises on X-ray diffraction, such as the classic work by Klug and Alexander [2].

Analysis by X-ray diffraction requires that a specimen be placed in the primary beam of a diffractometer and the diffraction angle and the intensity of each diffracted beam be measured. Diffractometers use either an electronic detector or photographic film to indicate the position of the diffracted beams of X-rays. Most diffraction units in industrial laboratories today use an electronic detector, usually a proportional counter. Figure 1 is a simplified diagram of a diffractometer. Here, the specimen is placed in a holder at the center of a goniometer system. A receiving slit and detector slowly sweep around an arc at a fixed distance from the center of the goniometer, facilitating determination of the intensity of X-rays scattered at each angle, 2θ, on the arc. While the detector moves through angle 2θ, the specimen rotates about the same axis through angle θ. A plot of the intensity of scattered radiation as a function of 2θ, a diffractogram or diffraction pattern, is thus produced. Figure 2 shows the diffraction pattern of the rutile form of titanium dioxide.

A relatively new variation of the electronic detector is the position-sensitive detector (PSD) that uses an arc-shaped solid state detector to sense both the position and intensity of the diffracted radiation [6,7]. The PSD is stationary during data collection, but may be moved to different locations on the goniometer circle, as required, so that its surface can intercept X-rays at all 2θ positions of interest. Compared to a conventional scanning unit, a PSD can markedly shorten the time required to collect data.

The oldest method for collection of diffraction patterns, photographic, is still useful today, with the Debye-Sherrer camera being the most commonly used camera [2]. The Debye-Sherrer camera (Fig. 3) uses a strip of film mounted on the inner surface of a cylindrical holder. The film records X-rays diffracted over a 2θ range of 360°. The d-spacing of arcs caused by exposure of the film to diffracted X-rays can be calculated from the position of the arcs on the film. Relative intensities of the diffracted X-ray beams can be evaluated by measuring the degree of darkening of the corresponding arcs on the film by an optical density measurement or by visual comparison to standards. Figure 4 shows the diffraction pattern of rutile TiO_2 recorded with a Debye-Sherrer camera.

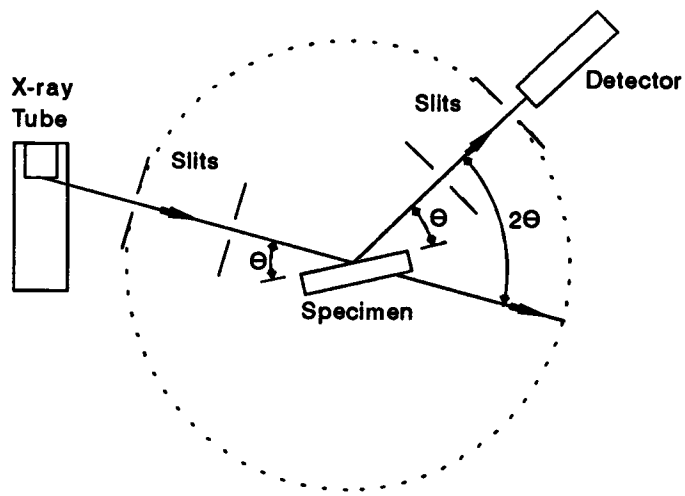

FIG. 1—X-ray diffraction goniometer system.

Experimental Procedure

Specimen Preparation

Specimens for X-ray diffraction can be any crystalline containing solid that can be mounted to permit collection of a diffraction pattern. For scanning diffraction units, the surface of the specimen should be flat and must be positioned in the focal plane of the instrument's X-ray optical system. The latter requirement can be met by mounting the specimen with its surface flush with the face of the specimen holder designed for the instrument. Failure to do so causes a systematic error in the observed 2θ angle and d-spacing of all peaks in the diffraction pattern. Figure 5 shows a photograph of specimen holders used in some commercial X-ray diffractometers.

Common types of samples encountered in the coatings industry and the recommended modes of mounting them in a scanning diffractometer are summarized in Table 1.

A Debye-Sherrer camera is useful for analysis in cases where there is too little sample for analysis using a conventional scanning diffraction unit. For small amounts of powder, the specimen is prepared by loading the powder into a thin-walled glass capillary or by mixing the powder with noncrystalline glue and rolling the mixture to form a filament. The capillary or filament after hardening is mounted in the center of the camera on a motor-driven rotating stub. Rotation presents a more nearly random orientation of crystallites to the incident X-ray beam. A single small chip or crystal may be analyzed by attaching it by glue to the end of a

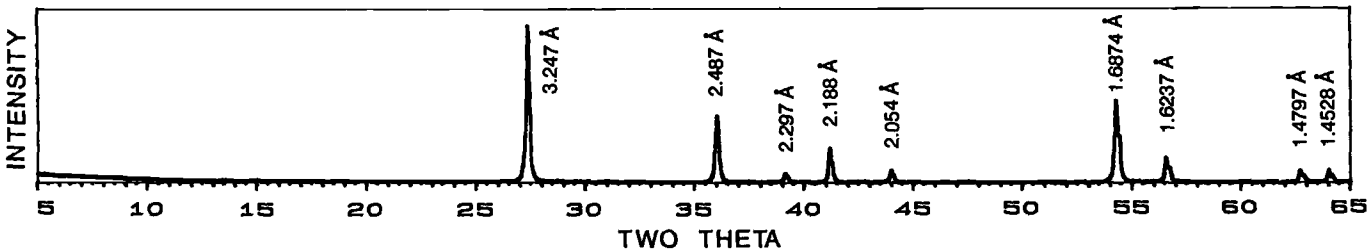

FIG. 2–X-ray diffraction pattern of rutile TiO_2 with the peaks labeled with the *d*-spacing of the corresponding sets of crystallographic planes.

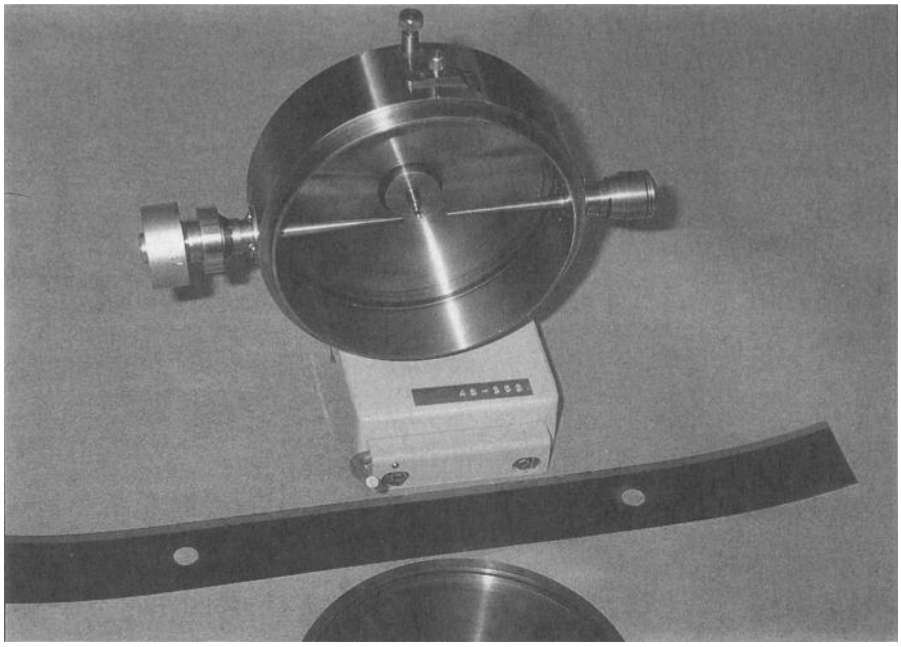

FIG. 3–Debye-Sherrer camera with the front cover removed displayed with a developed X-ray film.

glass capillary and exposing it to X-rays in the Debye-Sherrer camera. In Fig. 3, the capillary can be seen mounted along the axis at the center of the camera.

Specimens suitable for a Debye-Scherrer camera are equally suitable for XRD units equipped with a position-sensitive detector and a holder for capillary specimens.

A thin-film X-ray diffractometer, a variation of the scanning diffractometer, can be extremely useful in the analysis of thin films of crystalline coating or contaminant on flat surfaces [*8,9*]. They also give better results than conventional diffractometers when only a small amount of powder is available. Thin film units operate exactly as conventional scanning diffractometers except the surface of the specimen is irradiated with X-rays at a fixed but selectable grazing angle. In comparison to conventional X-ray diffraction analysis, this approach reduces the depth of penetration of the X-ray into

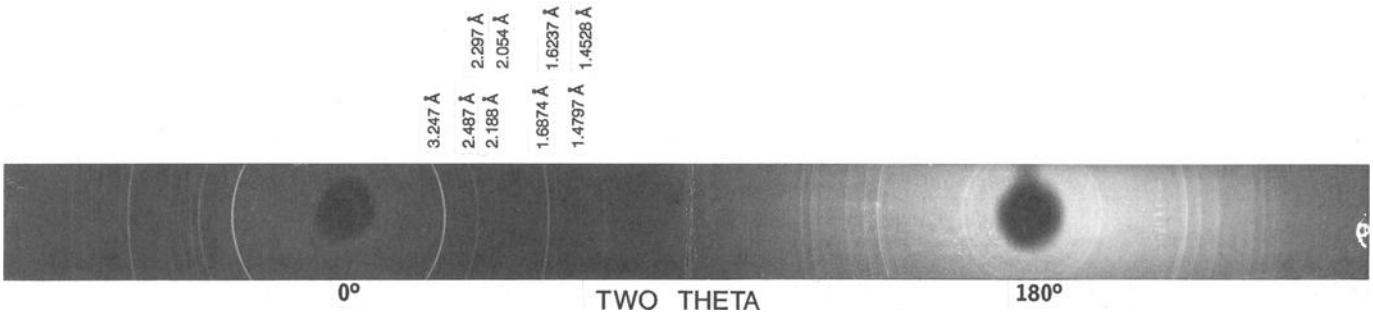

FIG. 4–Debye-Sherrer film with diffraction pattern of rutile TiO_2. The *d*-spacings of selected diffraction arcs are marked for comparison with peaks shown in Fig. 2.

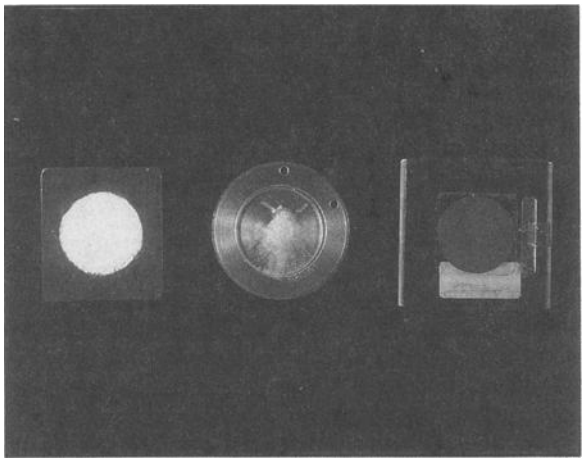

FIG. 5–Specimen holders for three common commercial X-ray diffractometers, each with a different type of specimen: (left) powder in a depression, (center) powder sprinkled on petroleum jelly smeared on a zero background quartz plate, and (right) disk cut from a drawdown of paint.

TABLE 1—Common samples and method of mounting for XRD analysis.

Sample	Method of Mounting
Powder	Put directly in holder or sprinkle on film of petroleum jelly or amorphous glue on zero background plate.
Liquid paint or grind paste	Prepare drawdown film on amorphous plastic sheet. Cut specimen to fit holder. Attach specimen to holder using double stick tape.
Paint chip	(1) Cut specimen to fit holder or (2) scrape off portion of interest, pulverize, and run as powder.
Paint on panel	Cut specimen to fit holder or cut to same dimensions as holder and run without holder.
Pretreatment on metal	Cut specimen to fit holder or cut to same dimensions as holder and run without holder.
Paint with low pigment content	Remove pigment from paint by centrifugation. Dry and grind the pigment plug. Mix the ground material. Run as powder.[a]
Suspension in liquid	Isolate solids from liquid by decantation, filtration, or centrifugation. Dry, grind, and mix. Run the resultant powder as described above.[a]
Sludge	(1) Run as drawdown on amorphous plastic sheet or (2) dry, grind, mix, and run as a powder.
Gel	(1) Run as smear on plastic sheet, (2) dissolve organic portion with solvent and then handle sample as suspension, or (3) ash and handle as powder.[b]

[a]*Caution:* The composition of the plug may be heterogeneous because of stratification of pigments during gravity settling or centrifuging.

[b]*Caution:* Ashing may change the crystalline composition of a sample by causing decomposition, vaporization, or transformation of phases that are present. Ashing at mild temperature, 450°C, in accordance with ASTM D 4451-85, Test Methods for Pigment Content of Paint by Low Temperature Furnace Ashing (450°C), may prevent or lessen the amount of change of crystalline components [23].

the specimen and enhances the strength of the signal from crystalline components on the surface [9].

Instrument Operation Conditions

Operating conditions should be based upon recommendations of the manufacturer of the X-ray diffraction unit, requirements of the analytical method being used, and practical laboratory considerations. As a general rule, X-ray tubes with copper targets are commonly operated with a potential of about 40 to 45 kV and a filament current of about 35 to 45 mA. If other factors are held constant, then higher power settings can be used to shorten analysis time, lower the limit of detection, and improve signal-to-noise ratio, but at the expense of shortened tube life. For routine, general-purpose analysis by scanning X-ray diffraction units, the common choice for slits used to define the dimensions of the X-ray beam illuminating the specimen and reaching the detector are as follows: 0.15° for the receiving slit and 1.0° for all other slits. If other factors are held constant, then larger slits can be used to shorten analysis time, lower the limit of detection, and improve signal-to-noise ratio, but at the expense of reduced ability to resolve closely spaced peaks. Conversely, smaller angle slits should be used if higher resolution is required. For analysis of unfamiliar paints, pigments, and other materials, diffraction patterns should be collected over a range scanning at least from 5 to 65° 2θ. Use of a shorter scan range may cause the omission of important diffraction peaks. However, scans spanning a narrow 2θ range may be satisfactory for routine tests based on peaks located within a chosen portion of the diffraction pattern. For routine qualitative and semiquantitative analysis, satisfactory results can be achieved with most step scanning instruments by progressing in steps of 0.02° 2θ, with 1.0 to 1.2 s per step. Longer count time may be required for quantitative analysis. In the case of older diffractometers with analog scanning motors, a scan rate of 1°/min is satisfactory for routine qualitative and semiquantitative analysis.

Qualitative Analysis

Interpretation of X-ray Diffraction Patterns

Preparation of d-Spacing Intensity Table—After the X-ray diffraction pattern of a test sample is recorded, the analyst must obtain a list of all diffraction peaks with their *d*-spacing and relative intensity. The peaks should be listed in descending order of *d*-spacing. The intensity is expressed as a percentage of the strongest peak, taken as 100. If the X-ray unit lacks data processing capability, then the analyst must read the 2θ of each peak from the pattern and calculate the *d*-spacings from the 2θ values of the peaks using the Bragg equation. Likewise, the height of each peak must be measured by hand and the relative intensity determined. However, *d*-spacing-intensity tables can be obtained automatically from diffraction units equipped with even the most basic computer capabilities.

General Comments—Identification of pigments, extenders, and other crystalline phases by X-ray diffraction is accomplished by matching the peaks of the diffraction pattern of a sample under analysis with the sets of diffraction peaks exhibited by reference samples of known composition [2,10,11]. X-ray diffraction provides no chemical information about a test sample other than the identification of each com-

ponent that is achieved when a full match of its set of peaks is found. Either manual or computer-assisted searches can be done. Manual methods rely on the numerical comparison of d-spacings and intensities of diffraction peaks. Recent computer search methods also begin by matching the d-spacings of peaks, but rely in part on the analyst to do visual matching of peaks on a video screen.

Several instrument manufacturers and after-market suppliers offer computerized search-match programs. Operated on personal computers, these programs use diffraction data files stored on compact disk or magnetic medium. The data files are available from the International Centre for Diffraction Data (ICDD), formerly known as the Joint Committee for Powder Diffraction Standards (JCPDS) [*12*]. Use of these computer programs and data files can greatly speed qualitative analysis [*13*].

Manual Search Procedures—Diffractionists who are experienced in the analysis of paints, but who do not have computerized search-match facilities, usually employ a qualitative analysis procedure that has the two following steps. First, the diffraction pattern is inspected for the presence of sets of peaks that are characteristic of commonly used pigments and extenders, or other phases suspected of being present. Sets of peaks found in the pattern that are suspected of resulting from common components are compared to the peaks on reference diffraction patterns. The comparison may be done directly by comparing diffraction patterns or indirectly by comparing the d-spacings and relative intensities calculated from reference patterns. Partial or even complete identification of components may be achieved by this procedure. Second, peaks that were not identified by the first approach are subjected to a systematic search using compilations of X-ray diffraction data, such as the Powder Diffraction File from ICDD. The first approach is most useful when the analyst, because of information available from other sources such as elemental analysis, the appearance, knowledge of the intended use of the paint, or experience, suspects the presence of certain crystalline components.

Figure 6 shows the X-ray diffraction patterns of several common paint pigments. For brevity, the term pigment will be used to mean both pigments and extenders. The pigments are readily distinguished from each other and from all other crystalline material by the positions of the peaks on the 2θ scale and by the relative intensities of the peaks. Since the diffraction pattern of each crystalline phase is unique, it may be used as a "fingerprint" for identification. The patterns in Fig. 6 were collected under identical conditions from powder specimens. Although some pigments originally gave patterns with greater peak heights, they are all plotted to about full scale for convenience.

Figure 7 shows diffraction patterns of dried paint films of two test paints of known composition. Each crystalline component in the paint film contributes its own set of peaks to the pattern, with the position and relative intensity unaltered by the other components. Resin and other noncrystalline components produce only a broad, weak hump in the baseline. Some crystalline components of the two paints represented by Fig. 7 can be identified by comparison with the diffractograms of individual pigments in Fig. 6.

Table 2 lists 37 pigments and extenders commonly used in paint, with the d-spacings and relative intensities of their five

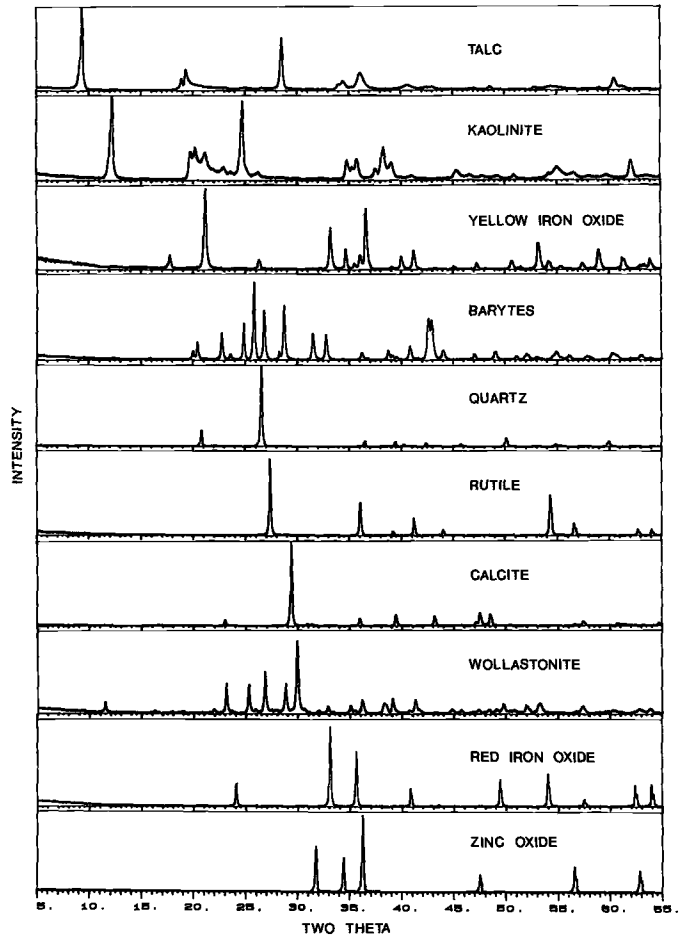

FIG. 6–X-ray diffraction patterns of several common pigments and extenders run as powder.

most intense diffraction peaks. This table, compiled from the Powder Diffraction File of ICDD, may aid the paint analyst in identifying common components. The pigments are listed in order of the d-spacing of the strongest peak. The d-spacing of the strongest peak is listed in the first column on the left. The next four strongest peaks of each phase are listed in decreasing order of their d-spacings. The subscripts state the relative intensity of each peak rounded off to the nearest integer, with the intensity of the strongest peak taken as 10 and represented by "x."

To use Table 2 in a systematic manner in interpreting a diffraction pattern, the analyst determines the d-spacing of the peaks at the high d-spacing end of the pattern of the sample under analysis and then searches the first column of Table 2 for apparent matches. When an apparent match is found for a peak, the pattern of the test sample is inspected for the presence of the remainder of the peaks listed in the same row of Table 1. The absence from the pattern of any one of the listed peaks is usually sufficient reason for rejection of the suspected component. However, in the case of materials consisting of platelet or acicular-shaped particles such as clays, mica, and aluminum flake, preferred orientation may greatly decrease the intensity of some diffraction peaks compared to the intensities listed in Table 2. If the pattern of the test sample has all the peaks listed for the candidate compo-

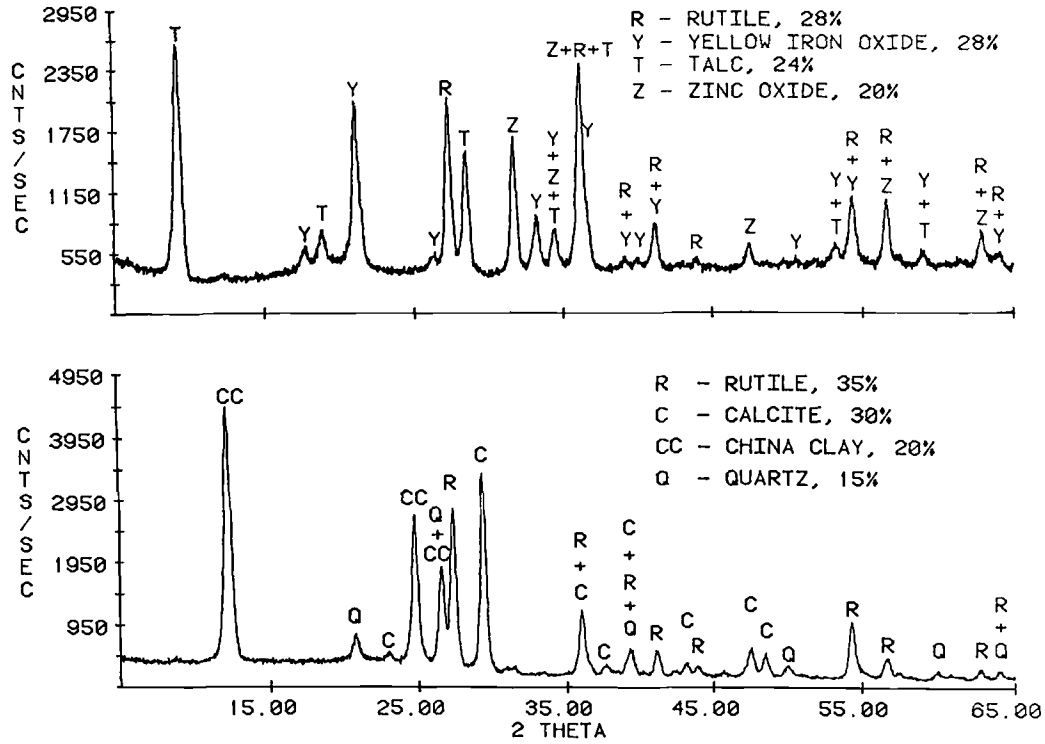

FIG. 7–X-ray diffraction patterns of drawdowns of two paints with the principal peaks of the constituent pigments labeled.

nent, then the analysts should note the ICDD file number listed for the phase in the last column. The file number may then be used to locate the full set of diffraction data provided by ICDD (and JCPDS) compilations. Using the ICDD data, all peaks attributed to the identified component may be marked on the pattern of the test sample. The identification process is then repeated with unassigned peaks in the pattern, working progressively from the peaks with the highest *d*-spacing, particularly the strongest ones, to the peaks with low *d*-spacing.

In an alternative use of Table 2, the analyst searches the list for crystalline phases that he suspects may be present in the test sample. If the strongest peaks listed in Table 2 for the suspected component are present in the diffraction pattern of the test sample, then the analyst notes the ICDD file number and proceeds as described in the previous paragraph.

The printed Alphabetical Index & Search Manual and its computer compact disk counterparts from ICDD provide an alphabetical listing by name of a large collection of crystalline phases, their formula, the *d*-spacing and relative intensity of the three strongest peaks, and their ICDD file number. These references are an extremely useful starting point in peak identification when the analyst knows or suspects the presence of certain phases in the test sample. If the three strongest peaks of a candidate are found in the pattern of a test sample, then the analyst should use the ICDD file number to locate the full set of diffraction data on the compact disk or in the equivalent printed volumes. For positive identification, all peaks listed for the candidate in the full data set must be present with appropriate intensity in the test pattern. However, the weaker peaks of a low-concentration component may be unobservable.

Peaks that remain unassigned after the information in Table 2 and the alphabetical files has been used must be identified by using the ICDD Powder Diffraction Files and either the Hanawalt or Fink search methods, or other search system. The Hanawalt method is based on the three strongest peaks in the diffraction pattern. The Fink method is based on the eight strongest diffraction peaks of each phase without use of intensity information. The Fink index lists each phase eight times with a cyclic permutation of the eight peaks. Instructions in the Hanawalt and Fink search manuals should be studied carefully before attempting to use either method [*12*]. Although still used in many laboratories, sale of Fink search manuals has been discontinued.

Computer-Assisted Searches—Analysts using computer programs for qualitative analysis must rely on instruction from the program supplier. In general, computer search routines provide a list of crystalline phases that have peaks that match, or approximately match, the 2θ positions of the peaks of the test sample. Unfortunately, since more than one phase, perhaps many, may have peaks at the same 2θ position as the test sample, a search-match program may suggest phases that are not actually present. "False hits" are especially common when the diffraction pattern of the test sample is complex. Recent computer search routines provide the opportunity for the analyst to include information about elemental content of the sample and a variety of additional physical and chemical data to exclude implausible candidates. They also permit the analyst to adjust the *d*-spacing range spanning each test sample peak to account for possible error in the *d*-spacings of test sample and reference data. The analyst can widen the *d*-spacing "search window" to reduce the possibility of missing a component of the test sample or

TABLE 2—Common pigments and extenders for paint.

d-Value and Intensity[a]					Name	Formula	ICDD File No.
17.6_x	9.0_5	4.49_8	3.58_4	1.504_6	bentonite[b]	$Na_{0.3}(AlMg)_2Si_4O_{10}(OH)_2 \cdot H_2O$	12-219
10.1_x	4.49_9	3.66_6	3.36_x	2.565_9	mica[b]	$KAl_2Si_3AlO_{10}(OH)_2$	7-25
9.34_x	4.66_9	3.116_x	2.476_7	1.870_4	talc[b]	$Mg_3Si_4O_{10}(OH)_2$	13-558
7.63_x	4.283_x	3.065_8	2.873_5	2.685_4	gypsum	$CaSO_4 \cdot 2H_2O$	33-311
7.36_x	4.56_5	3.66_8	2.451_7	1.531_7	chrysotile-20rcl	$Mg_3Si_2O_5(OH)_4$	25-645
7.31_x	4.57_5	3.65_7	2.27_3	1.535_5	chrysotile-2Mcl	$Mg_3Si_2O_5(OH)_4$	31-808
7.17_x	4.366_6	4.186_5	3.579_8	2.495_5	kaolinite[b]	$Al_2Si_2O_5(OH)_4$	14-164
4.568_x	9.12_6	4.410_2	3.460_3	2.853_7	zinc phosphate[b]	$Zn_3(PO_4)_2 \cdot H_2O$	37-465
4.18_x	2.69_4	2.45_5	2.19_2	1.72_2	yellow iron oxide	$FeO(OH)$	29-713
4.040_x	3.136_1	2.841_1	2.487_1	2.486_0	crystobalite	SiO_2	39-1425
3.52_x	2.370_2	1.892_4	1.700_2	1.667_2	anatase	TiO_2	21-1272
3.445_x	3.319_7	3.103_x	2.121_8	2.106_8	barium sulfate	$BaSO_4$	24-1035
3.39_x	6.32_2	2.986_8	2.840_4	2.269_2	chrome orange	$Pb_2(OH)_2CrO_4$	8-437
3.38_x	2.903_5	2.787_5	2.632_3	1.755_3	red lead	Pb_3O_4	8-19
3.342_x	4.257_2	2.457_1	1.818_1	1.542_1	quartz	SiO_2	33-1161
3.310_x	3.129_8	2.926_9	1.9103_8	1.7642_5	zinc sulfide	ZnS	36-1450
3.28_x	4.96_3	4.38_3	3.48_6	3.03_7	lead chromate	$PbCrO_4$	8-209
3.260_x	9.79_6	5.771_2	4.251_2	3.130_5	lead oxide sulfate hydrate	$Pb_4O_3SO_4 \cdot H_2O$	29-781
3.260_x	3.452_8	3.006_6	2.543_6	2.308_5	strontium chromate	$SrCrO_4$	15-356
3.247_x	2.487_5	2.188_3	1.687_6	1.624_2	rutile	TiO_2	21-1276
3.22_x	4.89_3	4.72_3	3.12_x	2.668_2	moly orange	$Pb(Cr_{19}Mo_{11})O_4$	19-685
3.160_x	3.583_8	3.367_6	2.068_6	1.761_5	cadmium yellow	CdS	6-314
3.142_x	4.571_2	3.494_3	3.174_2	3.118_8	antimony oxide	Sb_2O_3	11-689
3.030_x	3.852_3	2.284_2	2.094_3	1.8726_3	calcite	$CaCO_3$	24-27
2.886_x	2.192_3	2.015_2	1.804_2	1.786_3	dolomite	$CaMg(CO_3)_2$	11-78
2.700_x	3.684_3	2.519_7	1.8406_4	1.6941_5	red iron oxide	Fe_2O_3	33-664
2.666_x	3.633_8	2.480_x	2.176_4	1.672_9	chrome oxide green	Cr_2O_3	6-504
2.623_x	4.47_6	4.25_6	3.61_9	3.29_9	lead carbonate hydroxide	$Pb_3(CO_3)_2(OH)_2$	13-131
2.609_x	7.02_9	3.31_9	3.08_9	2.896_7	zinc yellow	$K_2Zn_4(CrO_4)_2 \cdot 3H_2O$	8-202
2.5503_x	2.8766_3	2.3846_7	1.6361_4	1.4376_4	copper chromium oxide	$CuCr_2O_4$	34-424
2.543_x	2.984_4	2.109_2	1.624_3	1.491_4	tan iron oxide	$ZnFe_2O_4$	22-1012
2.532_x	2.967_3	2.0993_2	1.6158_3	1.4845_4	black iron oxide	Fe_3O_4	19-629
2.476_x	2.814_6	2.603_4	1.625_3	1.477_3	zinc oxide	ZnO	36-1451
2.443_x	2.864_7	2.026_2	1.5602_4	1.424_4	cobalt aluminum oxide	$CoAl_2O_4$	10-458
2.338_x	2.024_5	1.431_2	1.221_2	0.9289_1	aluminum metal[b]	Al	4-787
2.091_x	2.473_5	2.308_4	1.687_3	1.342_3	zinc metal[b]	Zn	4-831

[a]Subscripts represent the relative intensity (rounded to the nearest integer) of the diffraction peaks of a phase with the most intense peak taken as 10 and represented by "x."

[b]Particles of this material frequently exhibit preferred orientation in paint films, thus causing the observed relative intensities to differ significantly from intensities listed in this table.

narrow the window to reduce the number of false hits. When analyzing "difficult samples," the analyst may benefit from comparing the results of searches run with a variety of search window widths. Some search routines assign a figure of merit to each candidate on the list based on similarity between data for the test sample and the candidate. Most programs permit the analyst to suggest candidates for consideration and exclude specific noncandidates. The analyst may draw on his knowledge of the origin of the sample and use Table 2, when appropriate, to suggest candidates. Visual matching on a video screen of the 2θ position and intensity of peaks of candidate components, represented by "sticks," with the position and intensity of actual diffraction peaks is a key part of computer-assisted analysis. All candidate components with "extra" peaks not found in the diffraction pattern of the test sample must be rejected unless there is reason to suspect that preferred orientation of the particles can account for the discrepancy. Candidates with badly mismatched peak intensities must be considered suspect except when preferred orientation could account for the discrepancy. Relative intensities are especially unreliable for mineral pigments, especially clays, mica, and silica. Complete analysis ideally requires that a set of crystalline components can be identified that can account for all peaks, both their position and intensity, observed in the diffraction pattern of the test sample.

Although computer search-match programs are valuable aides for interpretation of diffraction patterns, common programs that are presently available may suggest the presence of components that are absent and fail to show the presence of phases that are truly present. Therefore, results thus obtained should always be verified and, if necessary, corrected by the analyst.

Limitations—Qualitative analysis by X-ray diffraction has three principal limitations. First, only crystalline phases can be identified. Noncrystalline components must be identified by other means. Second, different substances can be encountered that have similar diffraction patterns, at least in part. Misidentification can occur when the sample contains several

crystalline phases producing a complex pattern and diffraction is the only technique being used for analysis. Examples of potentially confusing coincidences or near coincidences are the strongest peaks of red lead, quartz, and zinc sulfide, with *d*-spacings of 3.38, 3.34, and 3.31 Å, respectively, a secondary peak of barytes at 3.319 Å, and a strong peak of mica at 3.36 Å. The 3.247 Å peak of rutile may conceal the 3.260 Å peak of strontium chromate. The 3.446 peak of barytes may conceal the 3.452 Å peak of strontium chromate. Many other similar peaks can be found for common pigments in Table 2. Third, low concentration components may be overlooked, especially if they scatter X-rays weakly or if their strongest peaks are overlapped by major components. For example, small amounts of zinc oxide may be overlooked if its strongest peak at 2.476 Å is overlapped by a peak of rutile at 2.487 Å or talc at 2.476 Å, particularly when the latter phases are major components. Fourth, the relative intensity of peaks in the pattern of certain phases may differ significantly depending on their history, the degree of preferred orientation of the particles, the specimen preparation techniques, and the instrument used to collect the pattern. Anomalies especially arise from pigments that consist of platelet or acicular particles that exhibit preferred orientation and from clays that have been changed by chemical, thermal, or mechanical processing.

The speed and reliability of analyses can be greatly improved if information is available about what elements and functional groups are present in the sample. X-ray fluorescence and optical emission spectroscopy are convenient techniques for qualitative elemental analysis. Plasma emission, atomic fluorescence, and atomic absorption spectrometry can also be used for elemental analysis. Infrared spectroscopy can provide functional group information and, through spectral matching, may provide independent corroboration of pigment identification. Elemental analysis data are particularly useful in detecting and identifying crystalline components that are present at low concentrations. Elemental analysis and infrared spectroscopy results are useful for identifying noncrystalline pigments.

Quantitative Analysis

Theory of Quantitation

Quantitative analysis by X-ray diffraction is based on the principle that the intensity of a diffraction pattern of a crystalline substance is directly proportional to the concentration of that substance in the sample. This relationship and several complicating factors are discussed in detail by Klug and Alexander [*2*]. The intensity of X-rays diffracted from a given set of crystallographic planes in component *i* in a mixture is given by the equation

$$I_i = K_i' f_i / \mu$$

where

I_i = the intensity of diffracted X-rays,
K_i' = a constant that depends on both the nature of component *i* and the characteristics of the apparatus,
f_i = the volume fraction of component *i*, and
μ = the absorption coefficient of the mixture.

Since the absolute intensity I_i is influenced by the composition of the matrix, the absolute concentration of an analyte cannot be determined unless a calibration curve is established with an internal standard.

However, using the "matrix flushing" method described by Chung, the *relative* concentration of crystalline components in a mixture can be determined without knowledge of the absorption coefficient [*14,15*]. This approach is based on the fact that all components under analysis are in the same matrix and thus are equally influenced by X-ray absorption. The intensity of X-rays diffracted from a component *i* is given by the equation

$$I_i = k_i X_i$$

where

k_i = a constant that depends on component *i* and the apparatus, and
X_i = the mole fraction of component *i*.

The ratio of the intensity of X-rays diffracted from two components *i* and *R* is given by the equation

$$\frac{I_i}{I_R} = \frac{k_i}{k_R}\frac{X_i}{X_R}$$

where

k_R = a constant that depends on component *R* and the apparatus, and
X_R = the mole fraction of component *R*.

The constants k_i and k_R indicate the relative efficiency of two materials in diffracting X-rays from given sets of crystallographic planes into the detector of the diffractometer. The relative value of k_i and k_R can be determined from the equation

$$\frac{k_i}{k_R} = \frac{I_i}{I_R}$$

by measuring the intensity of X-rays diffracted from two crystalline components *i* and *R* in a 1:1 binary mixture. Peak area, rather than height, should be used to represent intensity since the former is less influenced by differences in particle-size distribution. Quantitative analysis of a multicomponent mixture requires that the identity of all components be known. One component is arbitrarily chosen as an internal reference, *R*. Binary 1:1 by weight mixtures are prepared with the reference component and each of the other components. The intensity ratio I_i/I_R of a peak, usually the strongest, of each component is then measured. The ratio of the intensities of the diffraction peaks defines the k_i/k_R of each pair of components. The ratio k_i/k_R is called a reference intensity ratio or RIR [*16–20*]. Corundum, the most commonly used reference material, is the basis of all RIR values given in ICDD Powder Diffraction Files. Davis, Smith, and coworkers published RIR values for some common materials, including several that are used as pigments or extenders in paint [*20,21*]. Published reference intensity ratios must be used with care since material other than corundum may have been used as the reference and intensity may have been measured as peak height instead of area.

PRACTICAL PROCEDURE FOR CALCULATING COMPOSITION

The relative weight percent of each crystalline components in a multicomponent mixture can be determined by the following procedure:

1. Determine the intensity of the diffraction peak chosen for quantitation of each component. (Integrated intensity based on peak area is recommended. Intensity may be expressed in counts per second, relative intensity compared to the most intense peak in the set, or any other consistent system.)
2. Determine the reference intensity (RIR) for every crystalline component in the sample if the information is not already available. (Once a RIR has been determined, it may be saved and used in future analyses conducted under the same experimental conditions.)
3. Divide the intensity of the chosen peak of each component by the corresponding RIR.
4. Normalize the set of quotients so that their sum is 100.
5. The normalized quotients correspond to the relative weight percent of each crystalline component.

Example:

The diffraction pattern of a sample indicated the presence of three components: rutile, quartz, and tan iron oxide. The analyst determined that the RIRs for these phases are:

3.20 for the 3.247 Å peak of rutile

2.96 for the 3.342 Å peak of quartz

2.32 for the 2.543 Å peak of tan iron oxide

The intensity of the corresponding peak for each component in the diffraction pattern of the test sample is:

Component	Intensity
Rutile	100.0
Quartz	19.1
Tan iron oxide	1.8

The data and calculated values may be organized as follows:

Component	Intensity	RIR	Quotient	Percent
Rutile	100.0	3.20	31.3	81.1
Quartz	19.1	2.96	6.45	16.8
Tan iron oxide	1.8	2.32	0.78	2.1

Two important points about quantitation by X-ray diffraction analysis should be noted. First, the results do not include noncrystalline components such as carbon black, amorphous silica, or highly processed clays. Second, the results do not represent percent by weight on either a dry film or a liquid paint basis.

The absolute weight percent of crystalline pigments and extenders can be determined by either:

1. Using a variation of the above method that includes an internal standard [*14,15,22*] added in known concentration to the paint.
2. Taking into account the total percent pigment in the paint if no amorphous pigment is present. The percent pigment in dry coating or water-reducible paint can be determined by ASTM Test Method for Pigment Content of Water Emulsion Paints by Low-Temperature Ashing (D 3723) [*25*]. The percent pigment in solvent-reducible paint can be determined by ASTM Method for Determination of Pigment Content of Solvent-Type Paints by High Speed Centrifuging (D 2698) or ASTM Test Method for Pigment Content of Solvent-Reducible Paints (D 2371) [*23*].

The accuracy and precision of quantitation by X-ray diffraction are strongly dependent on the number and type of crystalline components present, the accuracy of the reference intensity ratios used, the amount of preferred orientation of crystallites, and the instrument-operating conditions. Published studies reported that the "matrix flushing" method described above yielded results that agree with known composition within 4.2% relative for all components [*15*]. Standard deviations of about 0.4 and 5% have been reported for components comprising 90 and 5%, respectively, of three-part mixtures of NiO, α-Fe_2O_3, and Fe_2O_4 [*24*]. Smith et al. reported relative error ranging from 0 to 12% [*19*]. Dyakonov et al., in a study with seven laboratories, reported relative standard deviations of interlaboratory determinations ranging from 5 to 20%, but cited relative standard deviations of 60% for low-concentration components [*25*]. An approach for dealing with preferred orientation in mica has been suggested by Kamarchik and Ratliff [*26*].

Limitations

Quantitation of pigments by X-ray diffraction is sometimes handicapped by one or more of the following problems. First, the degree of crystalline regularity within particles of some pigments, especially silica and clays, may differ depending on the source and the nature of the processing that they have received. A factor contributing to variability of the apparent crystallinity is the amount of substitution of "foreign" ions in the crystalline lattice. An example is the substitution of magnesium for calcium in calcite and strontium for barium in barytes. Thus, a given amount of pigment in a test sample may diffract X-rays more or less strongly than the supposedly equivalent pigment sample used to establish the RIR. An article by Davis et al. provides a valuable listing of reference intensity ratios (*versus* corundum) for many common pigments and illustrates the variability of reference intensity ratios for pigments from different sources [*21*]. Second, pigments particles that are platelet or acicular in shape tend to assume preferred orientations in a paint film as the paint dries. If the extent of preferred orientation of the particles in the specimen and the reference specimen used to establish the RIR differs, then quantitation based on the RIR is incorrect. Mica and aluminum flakes commonly exhibit preferred orientation. Third, the strongest peaks normally used for quantitation may be overlapped by peaks of other components, thus requiring the use of weaker and less reliable peaks as the basis of quantitation.

Examples of X-ray Diffraction Analysis

Pigment Analysis

X-ray diffraction analysis is the most direct way to determine the identity and purity of pigments, whether in assessing the quality of pigments from established suppliers or in

evaluating pigment from potential new suppliers. Crystalline impurities contribute "extra" peaks to diffraction patterns, differences that may be readily seen in patterns of pigment powders alone or in grind pastes. X-ray analysis has long been established as the method of choice for determination of the amount of anatase in rutile [ASTM Test Method for Ratio of Anatase to Rutile in Titanium Dioxide Pigments by X-ray Diffraction (D 3720)] [*23*]. The widespread use of diffraction in the pigment industry attests to its utility in that field.

Questions concerning the identity or amount of pigments in paint can be more conveniently and definitively answered by X-ray diffraction than by any other technique. Visual comparison of diffraction patterns or, when necessary, quantitative analysis can be used to determine whether errors in pigment composition account for the difference in performance, color, or gloss of "good" and "bad" paint. Diffraction analysis is a basic tool that may be used to verify whether a paint that exhibits poor performance is the correct paint and comes from the correct supplier. The differences in the two patterns in Fig. 8, one for a good paint and one from a poorly performing suspect paint, coupled with differences in resin and solvent determined by other techniques, proved that the suspect paint was an unauthorized substitute.

Metal Pretreatment and Other Thin Coatings

X-ray diffraction can be used to determine the identity and amount of pretreatment on metal or, in general, crystalline coatings on substrate. Figure 9 shows the characteristic part of the diffraction patterns of two common types of pretreatment, hopeite [$Zn_3(PO_4)_2 \cdot 4H_2O$] and scholzite [$CaZn_2(PO_4)_2 \cdot 2H_2O$], on zinc-galvanized steel. Coating thickness or pretreatment weight can be determined by comparison of the intensity of one or more peaks of the species of interest with the same peaks exhibited by standard samples.

X-RAY FLUORESCENCE SPECTROSCOPY

Application

Types of Samples

X-ray fluorescence spectrometry is applicable to any liquid or solid that can be placed at the focal point of the X-ray optics system. Permissible specimen size differs widely with instrument type. Common commercial laboratory units can accept specimens as large as a cylinder about 4.0 cm in diameter and 2.5 cm in height to as small as 1 or 2 mg of powder. Some laboratory models can analyze specimens up to several centimeters in each dimension. There is no maximum size limit for bench top or portable units with hand-held X-ray probes.

Types of Information Provided

The most sophisticated and costly X-ray spectrometers can be used for qualitative and quantitative analysis of all elements in the atomic number range from 5 (boron) to 92 (uranium). Lower-cost instruments span fewer elements and offer less versatility.

Range of Concentrations

Analysis can be performed on elements ranging in concentration from 100% down to a few parts per million in favorable cases. The limit of detection differs widely with the

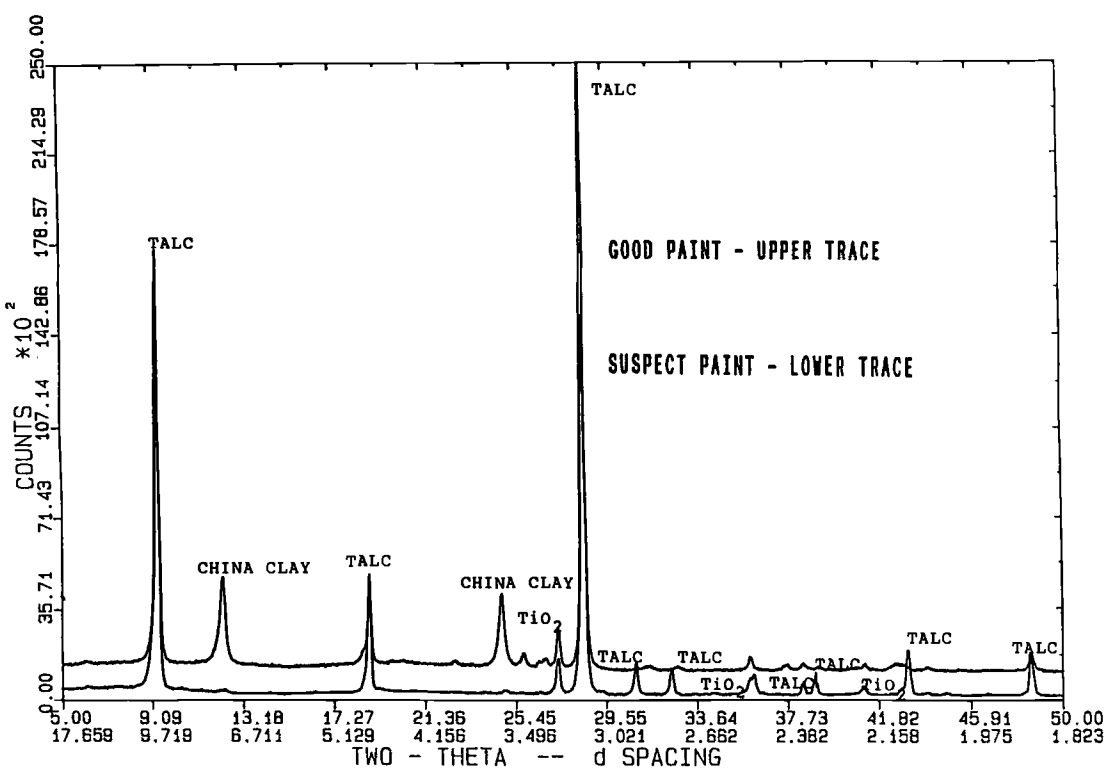

FIG. 8–X-ray diffraction patterns of drawdowns of two paints: one known to be good, one of suspect identity.

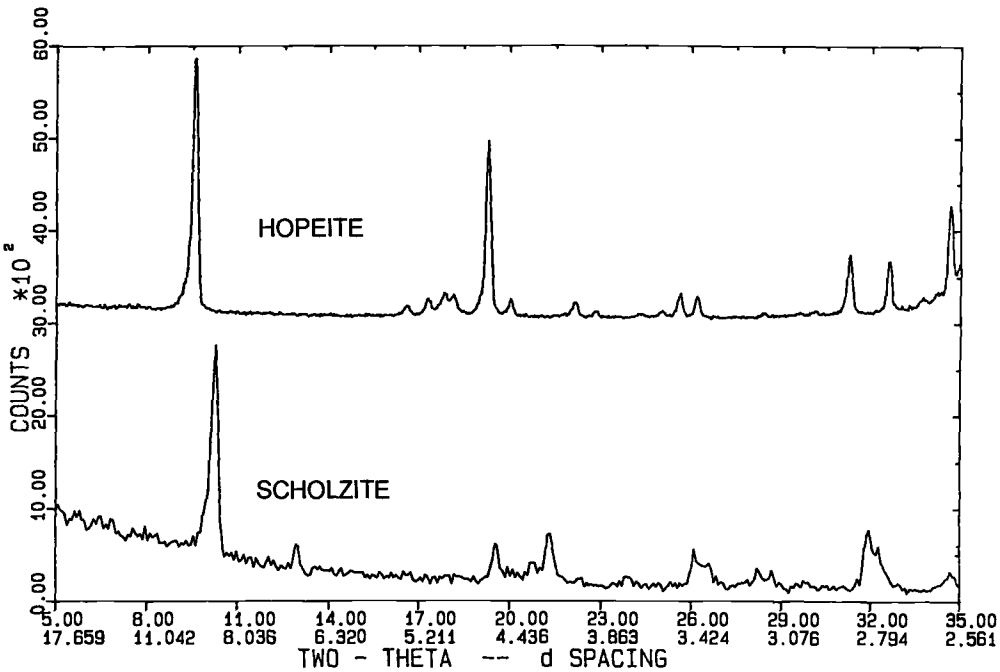

FIG. 9–X-ray diffraction patterns of hopeite and scholzite pretreatment on zinc-galvanized steel. (The principle peaks of zinc are beyond the right end of the pattern.)

model of spectrometer, the element of interest, and what other elements are present. The limit of detection rises rapidly with decreases in atomic number, especially below 11 (sodium).

Physical Basis

When X-ray photons of sufficient energy are directed onto a specimen, some photons are absorbed in a process that causes ejection of electrons from core atomic orbitals. The vacancies thus created in the inner orbitals are then filled by electrons from outer orbitals. The transitions of electrons from outer to inner orbitals are accompanied by the release of X-rays in a process called X-ray fluorescence [*27,28*]. The wavelengths of the fluorescent X-rays are greater than the wavelength of the incident X-rays. Of key importance in analysis is the fact that every element emits fluorescent X-rays at characteristic wavelengths. The spectra are plotted as intensity as a function of either 2θ angle (as in Fig. 10), wavelength, or photon energy (as in Fig. 11). Angle 2θ refers to the posi-

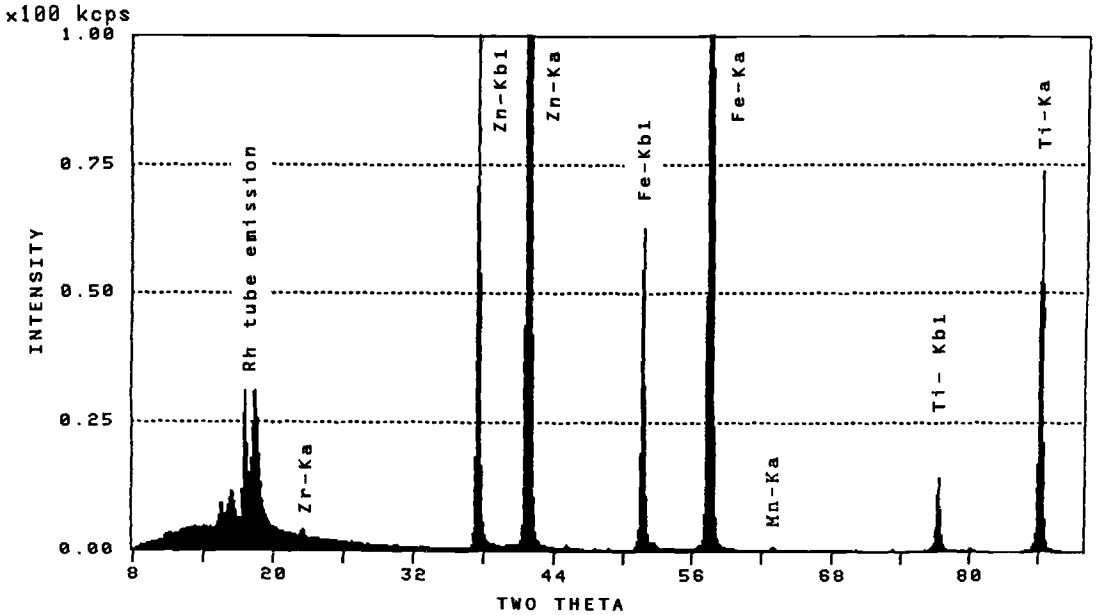

FIG. 10–Part of a WLD X-ray fluorescence spectrum of paint containing rutile, yellow iron oxide, talc, and zinc oxide.

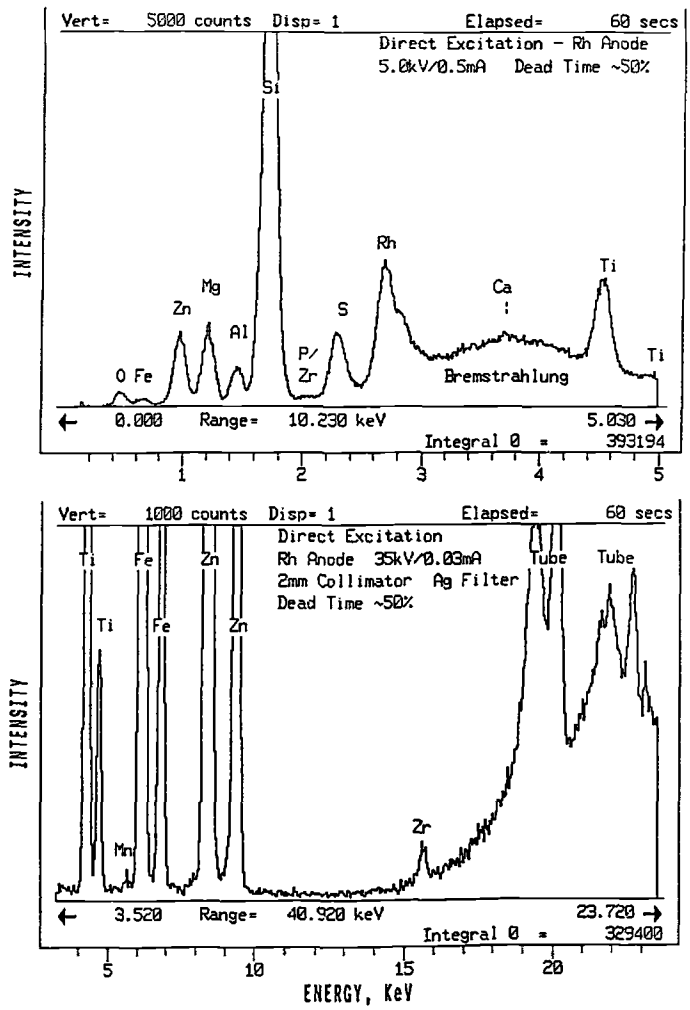

FIG. 11–X-ray fluorescence spectrum, recorded using an energy dispersive spectrometer, of the paint used for Fig. 10.

tion of the X-ray detector that moves at twice the angle of the diffraction crystal used in some instruments to separate different wavelengths to produce a spectrum.

Types of X-ray Fluorescence Spectrometers

Scanning

Scanning X-ray fluorescence spectrometers permit the acquisition of spectra spanning a broad wavelength or energy range. These spectrometers, usually floor-standing, are versatile instruments for both qualitative and quantitative analysis. Scanning spectrometers, most using X-rays from Coolidge-type tubes, can be further classified as either wavelength or energy dispersive.

Wavelength-dispersive (WLD) instruments produce a spectrum by using a crystal to diffract the fluorescent X-rays, a single wavelength at a time, onto a detector that measures their intensity. By rotating the crystal through an angle defined as θ as the detector moves around an arc through angle 2θ, only those X-rays that satisfy the Bragg equation reach the detector. The resultant spectrum is usually plotted as intensity as a function of 2θ angle, but could in principle be plotted as intensity as a function of wavelength. By use of several crystals, each effective for a certain span of wavelengths, a broad range of wavelengths can be scanned. Instruments based on energy-dispersive X-ray spectroscopy (EDXS) permit all wave lengths of the fluorescence to reach the detector simultaneously and use a pulse-height discriminator to electronically classify the energy of the X-ray photons that strike the detector.

Descriptions and comparisons of the two types of scanning spectrometers have been provided by Campbell [*29*]. Compared to EDXS units, the WLD spectrometers generally offer far superior resolution and lower limits of detection. EDXS instruments provide much faster acquisition of spectra and are usually lower in cost. Scanning spectrometers are convenient for qualitative elemental analysis and are broadly versatile for quantitative analysis [*30*].

Dedicated (Specialized Application)

Dedicated X-ray fluorescence spectrometers, available at much lower cost than the scanning spectrometers, permit quantitative analysis of a single element or a few selected elements. Most of the dedicated units, and all the lowest priced units, use a radioactive isotope instead of an X-ray tube as the source of radiation to excite the specimen [*31*]. In single element analyzers, the isotope source, detector composition, and operating conditions are chosen to give best performance for analysis of a specific element of interest. Dedicated X-ray spectrometers are typically small bench top units with simple operating procedures. They are well-suited for routine analysis [*30*].

On-line

Products and process materials may be analyzed on-line by specially adapted dedicated X-ray fluorescence units with remote analyzer heads [*32*]. The heads house the X-ray source and detector. Flow-through heads can be used for liquids. Fixed or moving heads can be used for moving sheet stock or other solid material. Bulk composition or the composition or thickness of a coating on a substrate can be determined by this method. The apparatus and methodology are custom-designed for each application.

Portable

Portable X-ray fluorescence units with self-contained power supplies and either single or multiple element capability are available for uses that require mobility. They are well-suited for rapid analysis in factory yards and in field studies [*33*].

Electron Beam Excited X-ray Spectroscopy

Spectroscopic analysis can be performed with X-rays generated by bombardment of a specimen with an electron beam, as in a scanning electron microscope (SEM) or an electron microprobe (EMP) [*27*]. The spectrum may be produced by either energy-dispersive or wavelength-dispersive means. SEM units, commonly equipped with energy-dispersive X-ray capabilities, are extremely useful tools for the study of surfaces and small features, especially defects such as craters, voids, pinholes, mars, and stains. In addition to providing images, such instruments can perform qualitative and quantitative elemental analysis. EMP units, usually equipped with both energy-dispersive and wavelength-dis-

persive capabilities, are used when the emphasis is on quantitation rather than imaging. Both SEM and EMP permit elemental analysis as point analysis, line scan, area analysis, or mapping. Present technology permits analysis of all elements with atomic number 4 (beryllium) and higher.

Experimental Procedures

Specimens may be any solid or liquid that can be presented to the X-ray beam. The size of the specimen holder of the spectrometer is the principal practical limitation. Sample preparation methods have been discussed by Bertin and Leyden [*27,34*]. Figure 12 shows two types of specimens.

Many of the recommendations given in Table 1 for X-ray diffraction also can be used to prepare specimens for qualitative analysis by X-ray fluoresence spectroscopy. However, the analyst is cautioned that the X-rays used for X-ray fluorescence spectroscopy are commonly more penetrating than those used for diffraction analysis. Unless care is taken, the fluorescence spectrum may show elements in the backing material used to support the intended specimen material. The analyst must either use a specimen that is sufficiently thick to prevent X-ray fluorescence from the backing from reaching the detector or use a backing (such as a metal-free polymer) that is free of conflicting elements. It is common practice to place liquid or powder in a disposable plastic cup, the bottom of which is covered with a thin plastic film that transmits X-rays. (Liquids and powder are most conveniently analyzed in spectrometers that irradiate the specimen from below. For instruments of the opposite configuration, the specimen cup must be filled so that there is no bubble when the cup is inverted in the analysis chamber.) Paint chips may be placed directly in the specimen cup, and drawdowns of paint on metal-free plastic sheets such as Mylar may be cut to fit the specimen holder.

For quantitation, powders may be pressed into disks in a binding agent such as orthoboric acid, granular cellulose, or graphite or cast as pellets after dissolution in molten flux such as lithium tetraborate or lithium metaborate. Ashing or extraction with acid or organic solvent is sometimes useful to remove analytes from bulky matrices, thus lowering the limit of detection and perhaps increasing analytical accuracy. Dissolution with acid or other solvent may make the sample more amenable to quantitation methods described under **Quantitative Analysis.** Detailed procedures for briquetting, fluxing, and ashing are available in the *Spex Handbook of Sample Preparation and Handling* [*35*]. Powders and liquids can be analyzed in disposable cups, as mentioned above. Disk-shaped specimens cut from solid samples may be handled in a similar manner. Bertin provides valuable information about specimen preparation [*27*].

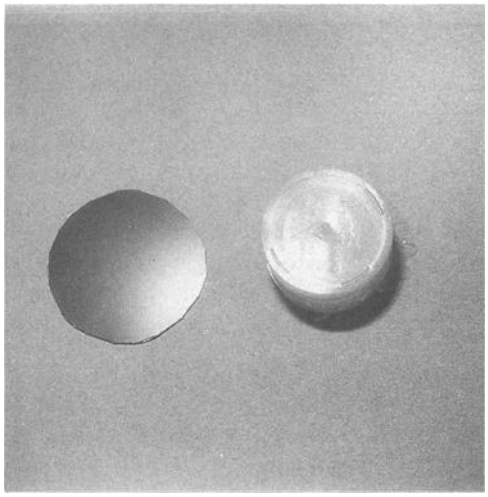

FIG. 12–Two examples of specimens: *left:* A disc cut from a painted steel aluminum; *right:* A plastic cup covered on the bottom with metal-free plastic film and on the top with a plastic cap. Suitable for liquids and powders.

Specimens are analyzed under vacuum whenever possible to minimize absorption of X-rays by the atmosphere in the analysis chamber. However, liquids and powders must be run under helium or air to prevent spatter. Portable analyzers and certain models of bench top units can operate without the specimen in vacuum or purge gas because of the short distance between the specimen and critical instrument parts.

Operating procedures differ widely with the make and model of X-ray spectrometer. Manufacturer instructions on safety and operation should be consulted.

Qualitative Analysis

Qualitative elemental analysis can be conveniently done using a scanning X-ray fluorescence unit. Elements in a specimen can be identified by the position of the peaks on the spectrum expressed as photon energy (kilovolts), 2θ angle, or wave length. Peak identification tables can be found in manuals provided by manufacturers of the spectrometers or in treatises on X-ray spectrometry [*27*]. Modern X-ray spectrometers have computer programs that can indicate what elements are present in a specimen. For instruction in use of these programs, the analyst should refer to the instrument operation manual.

Figure 10 shows part of an X-ray fluorescence survey spectrum (collected using a wavelength-dispersive instrument) of a drawdown of a tan paint, the same one used to produce the diffraction pattern in Fig. 7*a*. Note the corroborative nature of element content indicated in Fig. 10 and the identity of the pigments determined from the diffraction pattern in Fig. 7*a*. For comparison, Fig. 11 is an X-ray fluorescence survey spectrum, recorded by an energy-dispersive instrument, of the same sample.

Quantitative Analysis

General Principles

The principles of quantitative analysis by X-ray fluorescence spectrometry have been discussed in detail by many workers including Bertin [*27,28*]. The basic equations show that the intensity of the fluorescent X-rays is proportional to the amount of element that produced the X-rays, but is influenced by other factors such as the density and absorption coefficient of the specimen. Nevertheless, the linear proportionality between analyte concentration and fluorescence intensity shows that common analytical methods such as standard addition can be readily employed in X-ray spec-

trometry. Direct comparisons of concentration can also be made between samples that differ only in the amount of analyte of interest. Analyses by these simple methods can be done with small, low-cost, bench-top analyzers. Analysis of more than one element, especially in a matrix of variable composition, is best done with more sophisticated scanning spectrometers with suitable computers and software. Yet, some bench-top analyzers equipped with computers can determine the concentration of more than one element in matrices of variable composition. X-ray spectrometers must be programmed and calibrated by the analyst or the manufacturer for each analytical task before reliable quantitative analysis can be done. Recalibration must be done periodically.

Direct Comparison Method

Quantitation by direct comparison is done as follows. The analyst prepares or collects a set of three or more reference specimens that contain an element of interest at a range of known concentrations, but are otherwise essentially identical. Equal amounts of each specimen are placed in specimen cups or otherwise prepared for analysis. The analyst collects fluorescence intensity data for the element of interest from the set of samples and establishes a calibration plot of intensity *versus* concentration. Modern X-ray spectrometers with integrated computer capabilities can store the calibration plot for convenient use. When the spectrometer lacks computer capabilities, the analyst can construct the plot manually or use an external computer. Test samples of unknown composition are then run on the spectrometer under conditions identical with those used when the calibration samples were run. Intensity data from each test sample can be converted to concentration through use of either a manual or computer-stored calibration plot. To avoid extrapolation error because of unexpected plot curvature or other reasons, the range of concentration of the reference specimens should span the concentration of the specimens being analyzed. If the test specimen lies outside the range, then either the specimen should be diluted by a known amount to bring it "on scale" or the calibration plot should be extended with additional reference specimens. Operating instructions from the supplier of the spectrometer should be followed.

When applicable, direct comparison is usually the simplest and most convenient element quantitation method available. It can be done with even the simplest X-ray spectrometers. Most modern X-ray spectrometers can store several, perhaps many, calibration plots suitable for different applications.

Cautions: (1) If a specimen differs in matrix composition or physical state from the specimens used to establish the calibration plot, then the analytical results may be incorrect. Error can be large if the matrix of the test sample and the reference samples differ widely in absorptivity of X-rays. (2) The calibration curve may show a significant amount of curvature if the analyte and the matrix differ widely in absorptivity (e.g., tin in resin) and a wide range of concentrations is spanned. If the intensity *versus* concentration plots shows curvature, then either a polynomial fit must be used or another method of analysis must be employed. (3) Calibration plots tend to lose accuracy with time and must be replaced or corrected following manufacturer instructions.

Standard Addition Method

The method of standard addition can be used when no suitable reference samples are available to permit analysis by direct comparison. In this method, the analyst divides the test sample into at least three equal portions of known volume or weight. One of the divided specimens is retained for analysis with no further change. Each remaining specimen is "spiked" with the element of interest in a series of different known amounts. This method has convenient application only to liquids, and perhaps to powders, because of the need to mix uniformly the added component with the original material. The concentration of *added* analyte in each specimen is then calculated. The intensity of X-ray fluorescence of the analyte in each specimen is measured under identical conditions. The intensity of the analyte fluorescence signal is plotted as a function of added analyte concentration, as in Fig. 13. The data line of the graph is extrapolated to the point of interception (a negative number) on the concentration axis. The absolute value of the concentration intercept corresponds to the concentration of the original unspiked sample. Many modern X-ray spectrometers have computer programs that do the calculation.

Empirical Methods

The empirical methods require the use of a set of reference samples that span the concentration range of all elements of interest. All modern high-priced and most mid-price X-ray spectrometers can perform analyses using one or more variations of this approach when equipped with suitable software. The analyst must follow the instructions from the instrument supplier. Empirical methods are well suited for routine multielement analysis of large numbers of samples of the same type. A different program, with its own set of reference samples, must be established for each class of samples and choice of elements. High accuracy and precision are achievable when the reference samples properly represent the test samples.

Fundamental Parameter Methods

Fundamental parameter methods are set up by the analyst with a set of reference samples, each either a pure element or a simple compound with a high percentage of an element of interest. In general, all elements to be analyzed should be included in the setup. However, some instruments can interpolate the analytical response of omitted elements from similar elements that were included in the setup. Programs that permit analysis by one or more fundamental parameters methods can be purchased with most high-price and some mid-price instruments. The analyst must follow instructions from the instrument supplier. In principle, once a program is established, no further reference samples are needed. In practice, recalibration is needed when instrument repair, maintenance adjustments, or other factors change the instrument response. No standard samples, in the usual sense of the word, are needed for calibration. Fundamental parameters programs can be used to perform multielement quantitative or semiquantitative analysis of test samples of widely varied composition and unfamiliar nature. Accuracy varies with the task and the sophistication of the instrumentation and software.

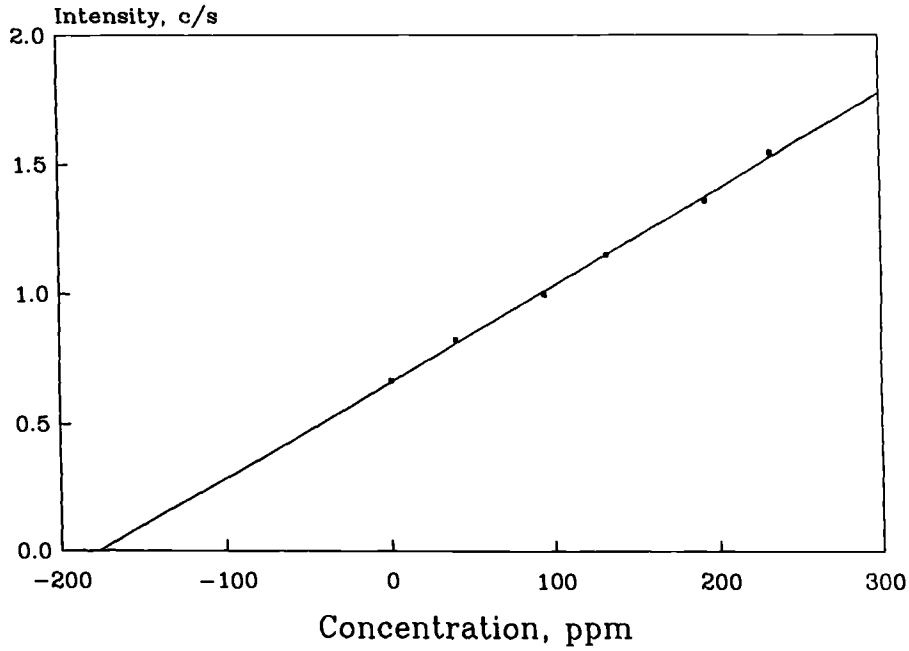

FIG. 13—A plot of the intensity of the sulfur K_α peak as a function of the concentration of sulfur in the analysis of an aqueous solution by a standard addition method.

Comparison to Other Techniques

In quantitative analysis of liquid samples, X-ray fluorescence spectrometry, compared to atomic absorption or plasma emission spectrometry, offers the advantage of being able to handle samples with (1) higher concentrations of analyte without use of large dilution factors and attendant inaccuracy, (2) matrices that are ill-suited for aspiration into nebulizers, and (3) elements that are not easily detected by flame or plasma photometric techniques.

Applications of X-ray Fluorescence Spectroscopy

Analysis of Elements in Solution

Figure 13 shows a plot of data used in the quantitation of sulfur in an acidic aqueous solution by a standard addition method. The sample resulted from flushing a steel panel retrieved from outdoor exposure with citric acid and then concentrating the solution by evaporation. This example illustrates a general-purpose method.

Surface Analysis

Foreign substances may sometimes be detected on surfaces by X-ray fluorescence spectroscopy, eliminating the need to resort to X-ray photoelectron spectroscopy and other "surface analysis" techniques. To be detectable, the contaminant must contain an element that is not present in significant amounts in the surface itself. Figure 14 shows a silicon peak in the high-resolution X-ray fluorescence scan of the surface of a piece of aluminum extrusion from which poorly adhering paint was peeled. Comparison of Figs. 14*a* and 14*b*, respectively, prove that washing the peeled surface with hexane significantly reduced the amount of silicon present. The elevated silicon signal on a substrate to which paint adhered poorly and the ready removal of the silicon material by hexane suggested the presence of silicone oil. This suspicion was confirmed using analysis by micro-infrared spectroscopy of residue left by evaporation of the hexane washings.

Detection of Bulk Contaminant

The low limit of detection of X-ray fluorescence spectroscopy makes it well suited for the detection of trace impurities, some of which may not be detectable by any other means. There is the tacit requirement that the contaminant contain an element that is not a normal component of the sample. Although small amounts of impurity may have no perceptible impact on the performance of a material, knowledge of the presence and amount of an impurity may be crucial in determining the cause of substandard performance. Table 3 summarizes data collected by X-ray fluorescence spectrometry in the investigation of a case in which silicone contamination was suspected as the cause of cratering exhibited by certain batches of water-borne paint. Quantitation was by a standard addition method. Although X-ray fluorescence spectrometry cannot distinguish between different silicon-bearing species, the higher level of silicon in batches of resin used in the crater-prone paint supports the suspicion that silicone caused the cratering. The data also suggest that a threshold concentration between 7 and 13 parts per million silicon in the resin is needed to produce cratering in the paint produced from it.

Quality Control

Dedicated X-ray fluorescence units that can determine the concentration of a single element have great utility in production plants for monitoring the composition of raw materials, intermediates, and products. One application is the monitoring of batches of paints to ensure compliance with federal regulations that limit lead content to no more than 600 parts per million based on nonvolatile content. A common tech-

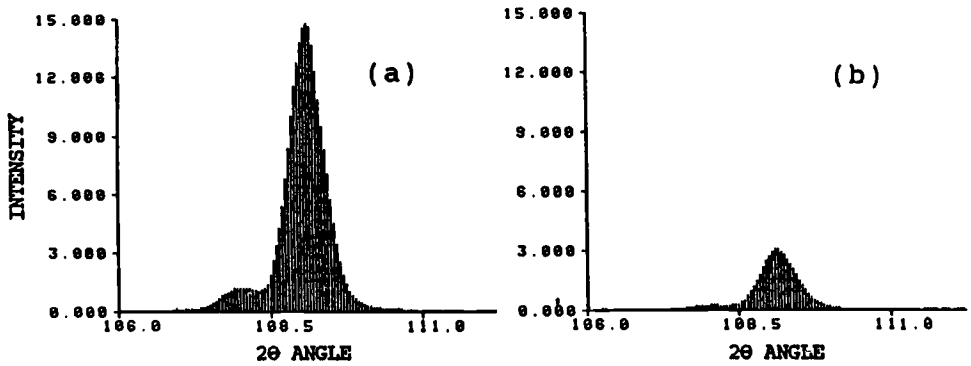

FIG. 14–The K_α peak of silicon on extruded aluminum from which poorly adhering paint has been peeled: (a) peeled only; (b) peeled and washed with hexane.

nique for determining lead content has been atomic absorption spectroscopy using ASTM Test Method for Low Concentrations of Lead, Cadmium, and Cobalt in Paint by Atomic Absorption Spectroscopy (D 3335) [*23*] or a similar method. X-ray fluorescence offers a quick alternative to atomic absorption spectroscopy, which may be too laborious and time-consuming for routine plant use. Lead content of a sample of paint can be determined by placing a drawdown or liquid specimen in the analysis chamber and directly reading either the content or signal count rate of lead. Dedicated X-ray fluorescence analyzers are available that give direct readout of concentration once a calibration curve has been established using samples of known concentration. The principal drawback of this method is the need for a separate calibration curve for every type of paint analyzed. Differences in the paint composition such as the type and amount of pigment can influence the intensity of the lead signal. In addition, interference from other elements such as bromine can produce large errors in apparent lead concentration.

Figure 15 is a plot of lead count rate from ten consecutive batches of paint measured with a dedicated X-ray fluorescence analyzer. The count rate that corresponds to 0.06% lead, the legal limit, is indicated by a horizontal line. To provide leeway for error, a lead limit of L_{max} (taking into account the precision of the method) may be chosen as the highest "passing" count rate. The dotted line represents L_{max}. Any sample that gives a count rate between L_{max} and the legal limit is considered suspect. Suspect batches of paint should be analyzed by ASTM Method D 3335 or other independent method, to determine the concentration of lead. Batches with unacceptable lead content may be scrapped or "blended-off."

TABLE 3—Concentration of silicone, determined by XRFS, in batches of resin used in batches of paint of known extent of cratering.

Extent of Cratering	Concentration of Silicon, ppm
None	3
None	4
None	7
Bad	13
Bad	13
Worst	40

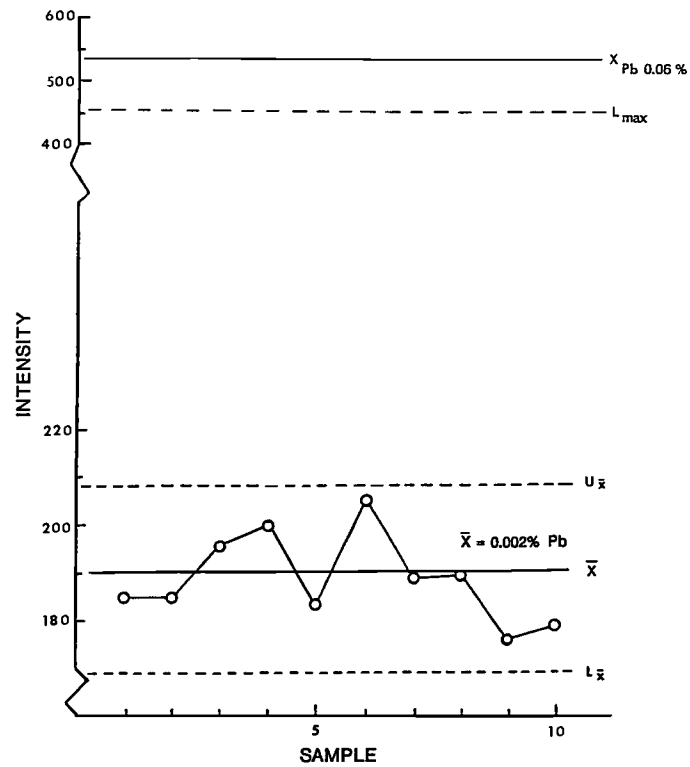

FIG. 15–A plot of the intensity of the lead signal for consecutive batches of latex paint as measured by a dedicated X-ray analyzer.

Dedicated X-ray analyzers have also been used to monitor the amount of rutile in batches of paint in production plants [*36*].

Guidance on the use of X-ray analyzers to determine the coating thickness is given in ASTM Standard Test Methods A 754-90, Coating Thickness by X-Ray Fluorescence [*37*], and B 568-90, Measurement of Coating Thickness by X-Ray Spectrometry [*38*].

Analysis in the Field

Concerns over the potential adverse health effects of lead in paint in residential buildings has prompted an interest in convenient, nondestructive methods of testing for lead. Fully portable X-ray analyzers that can detect lead in paint on walls

and other surfaces are commercially available. The analyzers can detect lead-containing paint beneath layers of lead-free paint, and some can provide direct readout of the amount of lead per unit area of paint surface [39]. The accuracy and precision are not well documented. The Department of Housing and Urban Development established a limit of 1.0 mg of lead per cm^2 of painted surface, a level detectable by portable analyzers.

Other uses of portable analyzers include determination of the weight of pretreatment on metal, the thickness of paint, and the concentration of key elements in samples at environmental cleanup sites.

SUMMARY

X-ray diffraction and X-ray fluorescence spectrometry, used alone or in combination, can provide valuable information about coatings, coating ingredients, impurities, and substrates. Sample preparation effort is minimal for both techniques. X-ray diffraction offers easy qualitative and quantitative analysis of crystalline materials in general and pigments in particular. X-ray fluorescence spectrometry is widely useful for qualitative analysis and, when suitable standards are used, for quantitative analysis. Attractive features of X-ray fluorescence spectrometry for quantitative analysis include its suitability for all elements except a few with lowest atomic number, applicability over a broad concentration range, tolerance of chemically reactive specimens, and applicability to samples of diverse physical states. Both X-ray diffraction and X-ray spectrometry are suitable for applications including basic research, product and process development, quality control, and practical problem solving. The area of greatest potential growth is the use of dedicated X-ray fluorescence spectrometers in production plants for quality control, particularly for on-line monitoring.

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Part 16: Specifications

Paint and Coatings Specifications and Other Standards

78

by Wayne Ellis[1]

MANY ORGANIZATIONS THAT PURCHASE paint products in large volume for maintenance and construction projects require conformance to their respective specifications. Such organizations may be federal, state, and local government departments and agencies, large industries, public utilities, railroads, and universities.

Briefly, a specification is a precise statement of a set of requirements to be satisfied by a material, product, system, or service that indicates the procedures for determining whether each of the requirements is satisfied [*1*]. Paints and coatings used in industrial new construction may be specified in construction documents, while paints used in maintenance may be described in individual specifications of the owner organization. Finishes applied by large manufacturing industries are often specified by their engineering departments. Specifiers of large quantities of maintenance finishes, such as public utilities, transportation organizations, and government agencies (local, state, and federal), purchase on a specification basis. Purchase may be by competitive bidding.

SPECIFICATIONS CONSIDERATIONS

The Construction Specifications Institute (CSI) [*2*] says the following items should be considered in a project construction specification: scope, related sections, references, definitions, performance requirements, submittals, quality assurance, delivery-storage-handling, project conditions, and sequencing scheduling. Submittals cover paint product data and color samples. Material specifications in the ASTM format [*3*] generally include terminology, ordering information, chemical composition, physical and mechanical properties, performance requirements, sampling, test methods or analytical methods, inspection, packaging and marking, and sometimes quality assurance. While this chapter deals mainly with standard specifications, others such as standard test methods, standard guides, standard practices, and standard terminologies, are often referenced in construction coatings operations. They include, for example, Federal Test Method Standards, which are available from Defense Printing Service Detachment Office (DPSDO).

Some paint and coatings specifications (for example, for military use) require prequalification of the products described. Such prequalification is required when the time to conduct tests will exceed 30 days, or when quality conformance inspection would require special equipment not commonly available, or when the specification covers life survival or emergency life-saving equipment. The specifications for these products include the requirements for qualification, the qualification tests, and the name of the activity responsible for qualification. Products that are qualified are listed on qualified products lists.

International specifications and standards for paint and coatings may be of interest. For example, Canadian standard 1-GP-71, *Methods of Testing Paints and Pigments*, may be obtained from the Canadian General Standards Board (Ottawa, Canada K1A 1G6, 819/956-0425). ISO (International Organization for Standardization) standards, such as the ISO 9000 series on quality performance, may be ordered from ANSI, the American National Standards Institute (1430 Broadway, New York, NY 10018 (212/642-4900) or directly from ISO (1, rue de Varembé, Case Postale 56, CH-1211 Genève 20, Switzerland, Telephone +41 22 749 01 11).

SOURCES OF PAINT SPECIFICATIONS

Federal Government Sources

The U.S. Department of Defense (DOD) *Index of Specifications and Standards (DODISS)* indexes government standardization documents (military specifications, standards, and handbooks; federal specifications, standards, and commercial item descriptions; qualified products lists; and industry documents adopted for DOD use); as well as alphabetic, numeric, and Federal Supply Class (FSC) listings. The *DODISS* is available to civil agencies and private sector industry by subscription, as either hardcopy from the Government Printing Office, or as microfiche from the Defense Printing Service Detachment Office (DPSDO) at 700 Robbins Avenue, Building 4D, Philadelphia, PA 19111-5094. Individual government documents may be ordered, generally without charge, from DPSDO; by telephone 215/697-2667, by fax 215/697-2978, or by mail from the Standardization Documents Order Desk, same address as previously stated. Automatic distribution of standardization document also is provided by DPSDO by subscription for new or revised issues in requested FSCs.

Non-Government Sources

Technical Societies

Committee D-1 on Paint and Related Coatings, Materials, and Applications of ASTM, the American Society for Testing

[1]Deceased, formerly of Harleysville, PA.

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TABLE 1—Construction/coatings criteria sources.

Organization	Address	Telephone	Fax	Criteria/services	Form
	Subscriptions 700 Robbins Avenue Building 4D Philadelphia, PA 19111-5094	215/697-2569 (DSN 442-) 7:30–4:30, ET	215/697-2978, 8–4, ET	DODISS subscriptions, industry/individuals; FSC subscriptions, industry/individuals	Microfiche Hardcopy
IHS	Informational Handling Services 15 Inverness Way East P.O. Box 1154 Englewood, CO 80150	303/790-0600 800/525-7052	303/397-2747	Standards and engineering data: government and industry standards, including coating materials; international and non-U.S. national standards; vendor catalog services	Microfilm, microfiche, compact disk system
GED	Global Engineering Documents 2805 Magaw Avenue Irvine, CA 92714	714/261-1455 800/854-7179	714/261-7892	National, non-U.S. national, and international standards; engineering data; technical publications	Hardcopy
GPO	Superintendent of Documents U.S. Government Printing Office Washington, DC 20402	202/783-3238 202/512-2303 (assistance)	202/512-2233	DODISS—government civil agencies and industry/individuals (subscription)	Hardcopy
GSA	GSA Specifications Unit, Suite 8100 4700 L'Enfant Plaza Washington, DC 20024	202/755-0325	202/755-0285	Federal standardization documents (priced or otherwise)—industry/individuals	Hardcopy
MFMA	Maple Furniture Manufacturers Association 60 Revere Drive, Suite 500 Northbrook, IL 60062	708/480-9138	708/480-9282	Specifications for finishes for wood floors, and a floor finish list for conforming products	Hardcopy
NACE	National Association of Corrosion Engineers P.O. Box 281340 Houston, TX 77218-8340	713/492-0535	713/492-8254	Standards for corrosion control, coating materials and selection, application, and testing; with surface preparation standards, joint with SSPC, in development	Hardcopy, volume
NIBS/CCB	National Institute of Building Sciences Construction Criteria Base 1201 L Street, Suite 400 Washington, DC 20005	202/289-7800	202/289-1092	Construction specification system: guide specifications and related standards—codes; design, cost estimating, and reference criteria; CADD criteria; and product data	Compact disk system, with executable software
NPFD	Naval Publications and Forms Directorate 5801 Tabor Avenue Philadelphia, PA 19120-5099	215/697-2266 -5647 (DSN 442-) 8–4, ET (info only)	215/697-5914 7–3:30, ET	DODISS subscriptions—DOD* FSC subscriptions—DOD* (*Army via (SMCAR-BAC-S); DLA VIA (DLA-XPD))	Hardcopy, microfiche hardcopy

and Materials (1916 Race Street, Philadelphia, PA 19103, 215/299-5585) has developed more than 800 standard test methods and practices concerned with paints and coatings. They include standard specifications for many paint raw materials, although not for commercial paints. These standards are published as Vols. 6.01 through 6.04 of the *Annual Book of ASTM Standards* and are available as separate standards.

AAMA, the American Architectural Manufacturers Association (Suite 310, 1540 East Dundee Road, Palatine, IL 60067, 708/202-1350), publishes specifications for organic coatings for aluminum. AASHTO, the American Association of State Highway and Transportation Officials (444 N. Capitol Street NW, Washington, DC 20001, 202/624-5800), has developed standards dealing with highway materials of construction, including paints. MFMA, the Maple Furniture Manufacturers Association (60 Revere Drive, Suite 500, Northbrook IL 60062, 708/480-9138), publishes specifications for finishes for wood floors and a list of conforming floor finish products.

NACE, the National Association of Corrosion Engineers (1440 South Creek Drive, Houston, TX 77084, 713/492-0535), has developed standards covering corrosion testing, selection of corrosion-resistant materials, and the use of coatings to reduce corrosion. SSPC, the Steel Structures Painting Council (4400 5th Avenue, Pittsburgh, PA 15213, 412/268-3326), has developed paint specifications and other standards for the preparation of metal surfaces for painting, painting systems, and paint application. CSI, the Construction Specifications Institute (601 Madison Street, Alexandria, VA 22314-1791, 703/684-0300), has prepared several *SpecGuides* as part of construction documentation covering the preparation of technical specifications for paints and painting.

Underwriters Laboratories Inc. (333 Pfingsten Road, Northbrook, IL 60062, 312/272-8800) is used to obtain UL listing, classification, and recognition. Testing sites are also located in California, North Carolina, and New York.

Nongovernment standards that have been adopted by the DOD and that are listed in the DODISS are issued by the Navy Publishing and Printing Service Office to DOD activities only [*4*].

Electronic Database Sources

A powerful database, the Construction Criteria Base (CCB), is available in compact disc format by subscription from the National Institute of Building Sciences (1201 L Street NW,

TABLE 1—Continued.

Organization	Address	Telephone	Fax	Criteria/services	Form
SSPC	Steel Structures Painting Council 4400 Fifth Avenue Pittsburgh, PA 15213-2683	412/268-3326	412/268-7048	Standards for surface preparation, coatings, coatings systems, application, quality control, and contractor qualification; surface preparation standards, joint with NACE, in development	Hardcopy, volumes
AAMA	American Architectural Manufacturers Association 1540 E. Dundee Road, Suite 310 Palatine, IL 60067	708/202-1350	708/202-1480	Standards for architectural products, including organic coatings for aluminum	Hardcopy
AASHTO	American Association of State Highway and Transportation Officials 444 N. Capitol Street, NW, Suite 225 Washington, DC 20001	202/624-5800	202/624-5806	Standards for transportation materials, including traffic paints, and for highway bridges	Hardcopy, volumes
AIA	American Institute of Architects 1735 New York Avenue, NW Washington, DC 20006	202/626-7300	202/783-8247	Masterspec libraries (guide specifications)	Hardcopy, computerized services
ASTM	ASTM 1916 Race Street Philadelphia, PA 19103-1187	215/299-5585 (publications) 215/299-5400	215/977-9679	Standards for testing materials, products, systems, and services, including coating materials	Hardcopy, volumes
CSI	Construction Specifications Institute 601 Madison Street Alexandria, VA 22314-1791	703/684-0300	703/684-0465	Database, government guide specifications service, technical documents	Hardcopy, computerized services
DPSDO	Defense Printing Service Detachment Office	215/697-2667/ -2179, (DSN 442-) 7:30–4:30, ET	215/697-2978, 8–4, ET	Assistance—inquiries, status, customer numbers for telespec tape orders	
	Customer Service 700 Robbins Avenue Building 4D Philadelphia, PA 19111-5094	215/697-1187 thru -1197, (DSN 442-) (telespecs) 8A–10P, ET	215/697-2978, 8–4, ET	DODISS--military orders; MIL/FED standardization documents and DIDS—all requesters, generally without charge	Hardcopy

Suite 400, Washington, DC 20005, 202/289-7800). It includes the complete construction guide specifications of most federal government departments and agencies, as well as those of many nongovernment organizations. The model building codes also are accessible in CCB. It is a consolidated system that includes full copies of supporting documentation and the software needed to develop end-item contract specifications for projects, including:

- Applicable codes and regulations.
- Construction guide specifications, of major military departments and civil agencies.
- Design and estimating guidance documents.
- Materials, testing, and processing documents.
- Product data, available in full-color graphics.
- Built-in software for search and processing functions.

Accessible in the CCB are referenced military and federal specifications and standards, commercial item descriptions, together with referenced nongovernment specifications and other standards. These latter are included by agreements negotiated with the copyright owners. Subscription variations include read-only, or full print copy access.

Information Handling Services (IHS), (14 Inverness Way East, P.O. Box 1154, Englewood, CO 80150, 303/790-0600), is another general source for both government and industry specifications and other standards for coating materials. It provides direct access to current issues of referenced documents cited in guide specifications, including all military and federal specifications, qualified products lists, handbooks, and commercial item descriptions. International standards are also available, as are vendor catalog services. Subscriptions are available in microfilm cartridge or compact disc formats.

National Standards Association (NSA), (1200 Quince Orchard Blvd., Gaithersburg, MD 20878, 301/590-2300), provides an online index (DIALOG File 113) of all U.S. government and industry standards, specifications, and related documents, including cancelled military specifications and standards dating back to the early 1940s.

Library Sources

Some standardization documents, indexes, databases, and services listed above may be available in government, state, city, industry, university, or federal depository libraries.

Table 1 summarizes construction/coatings criteria sources, access, and types of information available [5].

REFERENCES

[1] ASTM Terminology, D 123-92.
[2] SpecGuide 09900, *Painting*, February 1988.
[3] *Form and Style for ASTM Standards*, 1989.
[4] DODISS Notice, Vol. 9, No. 91, 6 May 1991, p. 1.
[5] Source: Naval Construction Battalion Center, Port Hueneme, CA, 1992.

Appendix

VISCOSITY CUP

*Conversion Between Centistokes "V" and seconds "T":

K	0.875	2.80	10.09	13.26	23.56	1.590	4.18	10.23	15.13	27.27	0.266	0.744	2.48	4.62	7.40	23.60	0.85	2.32	5.39	18.9
C	993	747	587	673	744	1070	760	575	545	540	157	300	385	275	200	204	175	190	185	210
MIN. Cs	10	19	64	79	161	15	39	63	97	219	2	12	25	29	53	215	11	19	35	167
MAX. Cs	36	156	596	784	1401	78	238	604	899	1627	14	40	142	273	441	1413	48	136	320	1125
STD. OIL	G10	G60	G200	G200	G350	G35	G60	G100	G350	G350	G6	G10	G35	G35	G60	G200	G20	G35	G60	G200
TOLERANCE	3%	3%	3%	3%	3%	5%	5%	5%	5%	5%	4%	4%	4%	4%	4%	4%	2%	2%	2%	2%
Cs/SEC.**	1.3	3.3	10.5	13.9	24.2	2.0	4.5	11.0	15.5	27.0	0.4	1.0	2.8	5.0	7.6	25.0	0.9	2.5	10.3	19.0

CENTI-STOKES	GARDCO EZ (EQUIVALENT ZAHN) CUP 1	2	3	4	5	GARDCO ZAHN SIGNATURE CUP 1	2	3	4	5	GARDCO FORD DIP CUP 0	1	2	3	4	5	GARDCO/FISHER DIP CUP 1	2	3	4
											FORMULA									
	(EFFLUX TIME IN SECONDS)					(EFFLUX TIME IN SECONDS)					(EFFLUX TIME IN SECONDS)						(EFFLUX TIME IN SECONDS)			
7.5											42.2									
7.9											43.2									
8.3											44.4									
8.7											45.6									
9.1											46.8									
9.6											48.2									
10.0	39.9										49.6									
10.5	40.2										51.2						21.8			
11.1	40.6										52.8						22.3			
11.6	41.0										54.5	29.4					22.7			
12.2	41.4										56.4	29.9					23.2			
12.8	41.8										58.3	30.5					23.7			
13.5	42.2										60.4	31.1					24.3			
14.1	42.7											31.7					24.9			
14.8	43.2					31.0						32.4					25.5			
15.6	43.7					31.3						33.1					26.2			
16.4	44.3					31.6						33.9					26.9			
17.2	44.9					31.9						34.7					27.7			
18.0	45.5					32.2						35.6					28.5			
18.9	46.2					32.6						36.5					29.3			
19.9	46.9	20.3				32.9						37.5					30.2	14.3		
20.9	47.7	20.5				33.3						38.5					31.2	14.6		
21.9	48.5	20.7				33.7						39.7					32.2	14.9		
23.0	49.3	21.0				34.2						40.8					33.3	15.3		
24.2	50.2	21.2				34.6						42.1	18.3				34.4	15.7		
25.4	51.2	21.5				35.1						43.4	18.6				35.7	16.0		
26.7	52.2	21.8				35.6						44.8	18.9				36.9	16.5		
28.0	53.3	22.1				36.2						46.3	19.3	11.3			38.3	16.9		
29.4	54.4	22.4				36.8						47.9	19.7	11.5			39.8	17.4		
30.9	55.7	22.8				37.4						49.6	20.2	11.7			41.3	17.9		
32.4	57.0	23.1				38.1						51.4	20.6	12.0			42.9	18.4		
34.0	58.3	23.5				38.8						53.3	21.1	12.2			44.7	19.0		
35.7	59.8	23.9				39.5						55.3	21.6	12.5			46.5	19.6	10.1	
37.5	61.4	24.4				40.3	18.7					57.5	22.1	12.8			48.4	20.2	10.3	
39.4		24.8				41.1	19.0					59.7	22.7	13.1			50.4	20.9	10.6	
41.4		25.3				42.0	19.3					62.1	23.3	13.4			52.6	21.6	10.9	
43.4		25.8				43.0	19.6						24.0	13.7			54.9	22.4	11.2	
45.6		26.4				44.0	20.0						24.7	14.1			57.3	23.2	11.5	
47.9		27.0				45.1	20.4						25.4	14.5			59.8	24.0	11.8	
50.3		27.6				46.2	20.8						26.2	14.9			62.5	25.0	12.2	
52.8		28.3				47.4	21.2						27.0	15.3				25.9	12.6	
55.4		29.0				48.7	21.7						27.9	15.8	10.2			26.9	13.0	
58.2		29.8				50.1	22.1						28.9	16.3	10.5			28.0	13.4	
61.1		30.6				51.5	22.6						29.8	16.8	10.8			29.2	13.8	
64.2		31.4	11.4			53.0	23.2	11.3					30.9	17.3	11.1			30.4	14.3	
67.4		32.3	11.7			54.7	23.8	11.5					32.0	17.9	11.5			31.6	14.8	
70.8		33.3	11.9			56.4	24.4	11.7					33.2	18.5	11.8			33.0	15.4	
74.3		34.3	12.2			58.3	25.0	12.0					34.5	19.2	12.2			34.4	16.0	
78.0		35.4	12.4			60.2	25.7	12.2					35.8	19.9	12.7			35.9	16.6	
81.9		36.5	12.7	10.9			26.5	12.5					37.2	20.6	13.1			37.5	17.2	
86.0		37.8	13.0	11.1			27.2	12.8					38.7	21.4	13.6			39.2	17.9	
90.3		39.1	13.3	11.3			28.1	13.1					40.3	22.2	14.1			40.9	18.6	
94.8		40.5	13.7	11.5			29.0	13.4					41.9	23.1	14.7			42.8	19.4	
99.5		41.9	14.0	11.8			29.9	13.8	10.1				43.7	24.0	15.2			44.7	20.2	
104.5		43.5	14.4	12.1			30.9	14.2	10.4				45.6	25.0	15.8			46.8	21.1	
109.8		45.1	14.8	12.4			31.9	14.6	10.6				47.5	26.0	16.5			49.0	22.0	
115.2		46.9	15.2	12.7			33.1	15.0	10.9				49.6	27.1	17.1			51.3	22.9	
121.0		48.7	15.7	13.0			34.3	15.5	11.2				51.8	28.3	17.9			53.7	23.9	
127.1		50.6	16.2	13.4			35.5	15.9	11.5				54.1	29.5	18.6			56.2	25.0	
133.4		52.7	16.7	13.8			36.8	16.5	11.9				56.5	30.8	19.4			58.9	26.1	
140.1		54.9	17.3	14.2			38.3	17.0	12.2				59.1	32.2	20.3			61.7	27.3	
147.1		57.2	17.8	14.6			39.8	17.6	12.6				61.8	33.5	21.2				28.5	
154.4		59.6	18.5	15.0			41.3	18.2	13.0					35.1	22.1				29.9	
162.2		62.2	19.1	15.5	10.0		43.0	18.8	13.4					36.7	23.1				31.2	
170.3			19.8	16.0	10.3		44.8	19.5	13.9					38.4	24.1				32.7	10.2
178.8			20.5	16.5	10.6		46.7	20.3	14.3					40.2	25.2				34.2	10.6
187.7			21.3	17.1	10.9		48.6	21.0	14.8					42.0	26.4				35.9	11.0
197.1			22.2	17.7	11.2		50.7	21.8	15.4					44.0	27.6				37.6	11.5
207.0			23.0	18.4	11.5		52.9	22.7	15.9					46.1	28.9				39.3	11.9
217.3			24.0	19.1	11.9		55.3	23.6	16.5					48.3	30.3	10.1			41.2	12.5
228.2			24.9	19.8	12.3		57.7	24.6	17.2	10.3				50.6	31.7	10.5			43.2	13.0
239.6			26.0	20.5	12.7		60.3	25.6	17.9	10.6				53.0	33.2	10.9			45.3	13.6
251.6			27.1	21.3	13.1			26.7	18.6	11.0				55.5	34.8	11.4			47.5	14.2
264.1			28.2	22.2	13.5			27.8	19.3	11.4				58.2	36.4	11.9			49.8	14.8
277.3			29.5	23.1	14.0			29.0	20.1	11.8				61.0	38.2	12.4			52.2	15.5
291.2			30.8	24.1	14.5			30.3	21.0	12.3					40.0	13.0			54.8	16.2
305.8			32.1	25.1	15.1			31.7	21.9	12.8					42.0	13.6			57.4	16.9
321.1			33.6	26.2	15.6			33.1	22.8	13.3					44.0	14.2			60.2	17.7
337.1			35.1	27.3	16.3			34.6	23.8	13.8					46.1	14.9				18.5
354.0			36.7	28.5	16.9			36.2	24.8	14.4					48.4	15.6				19.4
371.7			38.4	29.7	17.6			37.8	26.0	15.0					50.8	16.3				20.3
390.2			40.1	31.1	18.3			39.6	27.1	15.6					53.2	17.0				21.3
409.7			42.0	32.5	19.0			41.4	28.4	16.2					55.9	17.8				22.3
430.2			44.0	33.9	19.9			43.4	29.7	16.9					58.6	18.7				23.4
451.7			46.0	35.5	20.7			45.4	31.0	17.7					61.5	19.6				24.5
474.3			48.2	37.1	21.6			47.5	32.5	18.5						20.5				25.7
498.1			50.5	38.9	22.5			49.8	34.0	19.3						21.5				26.9
523.0			52.9	40.7	23.5			52.2	35.6	20.2						22.5				28.2
549.1			55.5	42.6	24.6			54.7	37.3	21.1						23.6				29.6
576.6			58.1	44.6	25.7			57.3	39.0	22.0						24.8				31.0
605.4			61.0	46.7	26.9			60.1	40.9	23.1						26.0				32.5
635.7				49.0	28.1				42.9	24.1						27.3				34.1
667.4				51.3	29.4				44.9	25.3						28.6				35.8
700.8				53.8	30.8				47.1	26.4						30.0				37.6
735.8				56.4	32.2				49.4	27.7						31.5				39.4
772.6				59.1	33.7				51.8	29.0						33.0				41.4
811.3				62.0	35.3				54.3	30.4						34.6				43.4
851.8					37.0				56.9	31.9						36.3				45.6
894.4					38.8				59.7	33.4						39.1				47.8
939.1					40.6				62.6	35.0						40.0				50.2
986.1					42.6					36.7						42.0				52.7
1035.4					44.7					38.5						44.1				55.3
1087.2					46.8					40.4						46.3				58.0
1141.5					49.1					42.3						48.5				60.9
1198.6					51.5					44.4						51.0				
1258.5					54.0					46.6						53.5				
1321.5					56.6					48.9						56.1				
1387.5					59.4					51.3						58.9				
										FORMULA						FORMULA				

*Use conversions only with GARDCO viscosity cups having certified "C" or "K" values as shown.

**Cup midrange sensitivity stated in centistokes per efflux second.

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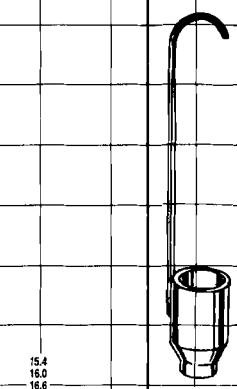
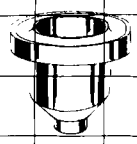
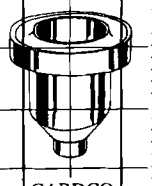
EQUIVALENT CHART©

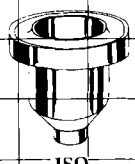
$$V = KT - C/T \text{ or } T = (V + \sqrt{V^2 + 4KC})/2K$$

GARDCO ISO DIP CUP 3 mm	GARDCO ISO DIP CUP 4 mm	GARDCO ISO DIP CUP 6 mm	DIN DIP 4 mm	GARDCO STANDARD FORD CUP 0	GARDCO STANDARD FORD CUP 1	GARDCO STANDARD FORD CUP 2	GARDCO STANDARD FORD CUP 3	GARDCO STANDARD FORD CUP 4	GARDCO STANDARD FORD CUP 5	GARDCO/ISO CUP 3 mm	GARDCO/ISO CUP 4 mm	GARDCO/ISO CUP 6 mm	GARDCO/ISO CUP 8 mm	DIN 4 mm	CENTI-STOKES
0.886	2.74	13.8	9.14	0.133	0.372	1.24	2.31	3.70	11.8	0.443	1.37	6.9	21.78	4.57	K
100	100	285	226	313	600	770	550	400	408	200	200	570	306	452	C
7	35	142	69	2	12	25	29	34	77	5	19	84	187	38	MIN. Cs
42	149	684	545	14	40	142	273	441	1413	52	163	823	2611	545	MAX. Cs
G10	G35	G100	G100	G6	G10	G35	G35	G60	G200	G10	G35	G100	G350	G100	STD. OIL
3%	3%	3%	3%	2%	2%	2%	2%	2%	2%	2%	2%	2%	3%	3%	TOLERANCE
1.0	2.8	14.2	9.4	0.2	0.5	1.4	2.5	3.8	12.5	0.5	1.4	7.1	22	4.7	Cs/SEC.**
FORMULA (EFFLUX TIME IN SECONDS)			FORMULA	FORMULA (EFFLUX TIME IN SECONDS)						FORMULA (EFFLUX TIME IN SECONDS)					
15.7				84.3						31.3					7.5
16.0				86.5						31.9					7.9
16.3				88.7						32.5					8.3
16.6				91.1						33.2					8.7
17.0				93.7						33.9					9.1
17.3				96.4						34.6					9.6
17.7				99.3						35.4					10.0
18.1				102.3						36.2					10.5
18.6				105.6						37.1					11.1
19.1				109.0	58.7					38.1					11.6
19.6				112.7	59.8					39.1					12.2
20.1				116.6	60.9					40.2					12.8
20.7				120.7	62.1					41.3					13.5
21.3					63.4					42.5					14.1
21.9					64.8					43.8					14.8
22.6					66.2					45.2					15.6
23.3					67.8					46.6					16.4
24.1					69.4					48.1					17.2
24.9					71.1					49.8					18.0
25.8					73.0					51.5					18.9
26.7					75.0					53.4	21.4				19.9
27.7					77.1					55.3	21.9				20.9
28.7					79.3					57.4	22.5				21.9
29.8					81.7					59.6	23.1				23.9
31.0					84.2	36.5				61.9	23.8				24.2
32.2					86.8	37.2				64.3	24.5				25.4
33.5					89.7	37.9				66.9	25.2				26.7
34.9					92.7	38.6	22.6			69.7	26.0				28.0
36.3					95.9	39.5	23.1			72.6	26.9				29.4
37.8					99.2	40.3	23.5			75.6	27.8				30.9
39.5					102.8	41.2	24.0			78.9	28.7				32.4
41.2					106.6	42.2	24.5			82.3	29.8				34.0
43.0	15.4				110.6	43.2	25.0			85.9	30.8				35.7
44.9	16.0				114.9	44.3	25.6			89.7	32.0			14.9	37.5
46.9	16.6				119.4	45.4	26.2			93.8	33.2			15.2	39.4
49.0	17.2				124.2	46.7	26.8			98.0	34.4			15.5	41.4
	17.9					48.0	27.5			102.5	35.8			15.8	43.4
	18.6					49.4	28.2			107.2	37.2			16.1	45.6
	19.4					50.8	29.0			112.1	38.7			16.5	47.9
	20.2					52.4	29.8			117.4	40.3			16.9	50.3
	21.0					54.1	30.6			122.9	42.0			17.3	52.8
	21.9					55.8	31.5	20.3			43.8			17.7	55.4
	22.9					57.7	32.5	20.9			45.7			18.2	58.2
	23.9					59.7	33.6	21.5			47.7			18.7	61.1
	24.9					61.8	34.7	22.2			49.8			19.2	64.2
	26.0					64.0	35.8	22.9			52.0			19.8	67.4
	27.2					66.4	37.1	23.7			54.3			20.3	70.8
	28.4					68.9	38.4	24.5			56.8			21.0	74.3
	29.7					71.6	39.8	25.3			59.4			21.6	78.0
	31.0					74.4	41.2	26.3	10.3		62.1			22.3	81.9
	32.5					77.4	42.8	27.2	10.6		65.0	17.3		23.1	86.0
	34.2					80.5	44.4	28.2	10.8		68.1	17.7		23.9	90.3
	35.7					83.9	46.2	29.3	11.1		71.3	18.3		24.7	94.8
	37.3					87.4	48.1	30.5	11.5		74.6	18.8		25.6	99.5
	39.1					91.1	50.0	31.7	11.8		78.1	19.4		26.6	104.5
	41.0					95.1	52.1	33.0	12.2		81.9	20.0		27.6	109.8
	42.9					99.2	54.3	34.3	12.5		85.8	20.7		28.7	115.2
	45.0					103.6	56.6	35.7	12.9		89.9	21.4		29.8	121.0
	47.2					108.2	59.0	37.2	13.4		94.3	22.1		31.0	127.1
	49.5					113.1	61.6	38.8	13.8		98.9	22.9		32.3	133.4
	51.9					118.2	64.3	40.5	14.3		103.7	23.8		33.6	140.1
	54.4	12.4				123.6	67.2	42.3	14.8		108.7	24.7		35.0	147.1
		12.8					70.2	44.2	15.3		114.0	25.6		36.5	154.4
		13.3					73.4	46.2	15.9		119.6	26.6		38.1	162.2
		13.9					76.8	48.3	16.5		125.4	27.7		39.7	170.3
		14.4					80.4	50.5	17.2			28.8		41.5	178.8
		15.0					84.1	52.8	17.8			30.0	10.0	43.4	187.7
		15.6					88.0	55.2	18.6			31.2	10.4	45.3	197.1
		16.3					92.0	57.8	19.3			32.5	10.8	47.4	207.0
		17.0					96.5	60.5	20.1			33.9	11.2	49.6	217.3
		17.7					101.1	63.4	21.0			35.4	11.7	51.8	228.2
		18.5					106.0	66.4	21.9			37.0	12.2	54.3	239.6
		19.3					111.0	69.5	22.8			38.6	12.7	56.8	251.6
		20.2					116.4	72.9	23.8			40.3	13.2	59.5	264.1
		21.1					122.0	76.4	24.9			42.2	13.8	62.3	277.3
		22.1						80.1	26.0			44.1	14.4	65.2	291.2
		23.1						83.9	27.2			46.1	15.0	68.4	305.6
		24.1						88.0	28.4			48.2	15.6	71.6	321.1
		25.3						92.3	29.7			50.5	16.3	75.1	337.1
		26.5						96.8	31.1			52.9	17.1	78.7	354.0
		27.7						101.5	32.6			55.4	17.9	82.5	371.7
		29.0						106.5	34.1			58.0	18.7	86.5	390.2
		30.4						111.7	35.7			60.7	19.5	90.7	409.7
		31.9						117.2	37.4			63.7	20.4	95.2	430.2
		33.4							39.2			66.7	21.4	99.8	451.7
		35.0							41.0			69.9	22.4	104.7	474.3
		36.7							43.0			73.3	23.5	109.9	498.1
		38.5							45.1			76.9	24.6	115.3	523.0
		40.3							47.3			80.6	25.8	121.0	549.1
		42.3							49.6			84.5	27.0		576.6
		44.4							52.0			88.7	28.3		605.4
		46.5							54.5			93.0	29.7		635.7
		48.8							57.2			97.6	31.1		667.4
									60.0			102.4	32.6		700.8
									62.9			107.4	34.2		735.8
									66.0			112.7	35.9		772.6
									69.3			118.3	37.6		811.3
									72.7			124.1	39.5		851.8
									76.3				41.4		894.4
									80.0				43.4		939.1
									84.0				45.6		986.1
									88.1				47.8		1035.4
									92.5				50.2		1087.2
									97.1				52.7		1141.5
									101.9				55.3		1198.6
									107.0				58.0		1258.5
									112.3				60.9		1321.5
									117.9				63.9		1387.5
									FORMULA				FORMULA		









Formula—Use formula to convert values beyond chart limits.
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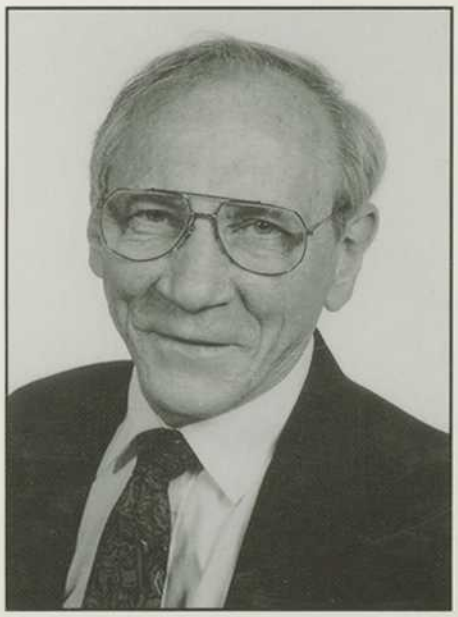
About the Editor



Dr. Joseph V. Koleske is a Senior Consultant for Consolidated Research, Inc., in Charleston, West Virginia. He has served in this capacity for seven years. Prior to this position, he was a Corporate Research Fellow at Union Carbide Corporation in South Charleston, WV for 25 years. In his career, he has worked in the areas of material science; solution properties of polymers, fibers, and polyurethanes; and radiation-curable, powder, and high-solids coatings.

He is a member of ASTM and the Federation of Societies for Coatings Technology and serves on the Editorial Review Board of the ***Journal of Coatings Technology.***

Dr. Koleske received his B.S. degree from the University of Wisconsin-Madison and M.S. and Ph.D. degrees from the Institute of Paper Chemistry, Lawrence College, Appleton, Wisconsin.

He holds 87 U.S. patents in the above fields and is the author or coauthor of more than 90 journal articles and book chapters. Co-authored books include ***Alkylene Oxides and Their Polymers,*** Marcel Dekker Inc., New York, 1990; ***Poly(ethylene oxide)***, Academic Press, New York, 1976; ***Poly(vinyl chloride)***, Gordon & Breach, New York, 1969.

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