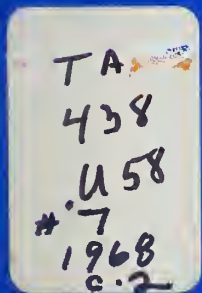# Organic Coatings

Properties, Selection, and Use

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards

Organic coatings in the form of paints, varnishes, lacquers, and related products are used for protective, decorative, and functional purposes on a wide variety of man's products—from children's toys to guided missiles. On rockets and spacecraft, paints provide identification, environmental protection, and temperature control.

Organic Coatings

Properties, Selection, and Use

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Abstract

This publication was prepared to fill the need for a comprehensive, unifying treatise in the field of organic coatings. Besides presenting practical information on the properties, selection, and use of organic coatings (and certain inorganic coatings), it provides basic principles in a number of important areas such as polymer structure, coatings formulation, pigment function, use of thinners, coating system compatibility, and theory of corrosion. Each chapter deals with a major area of the coatings field, including types of coatings, properties of synthetic resins, selection of coating systems, storage and safety, application methods, and surface preparation and pretreatment. There is also a consolidating chapter with illustrative examples of solutions to typical coatings problems. Interrelationships among the various areas of information are indicated through appropriate cross-referencing in the text. Specific references to Federal, Military, and other specifications are given where pertinent, and an entire chapter is devoted to a quick guide and summary of Federal specifications for organic coating materials. Finally, a selected bibliography and a comprehensive index are provided. While written primarily to meet the informational needs of the engineer, architect, maintenance superintendent, and responsible coatings procurement officer, the treatise is sufficiently broad in scope to serve as a general manual, a concise text, or a convenient reference source in the field of organic coatings.

Key words: application, coatings, coating systems, corrosion-inhibiting, Federal specifications, fire-retardant, lacquer, latex, multicolor, organic coatings, paint, pigments, polymers, properties, resins, selection, substrates, surface preparation, varnish, water-thinned.

Foreword

Since publication in 1945 of the Paint Manual issued as National Bureau of Standards Building Materials and Structures Report 105, there have been many significant technological advances in the field of organic coatings. Materials and techniques that were nonexistent or only dimly foreseen twenty years ago are now in daily use. Coatings with new and improved properties emerge continually from research laboratories and production lines. The task of choosing wisely from this huge array of materials is a complex and difficult one that requires both a knowledge of what is available and an understanding of where and how these materials and techniques can best be utilized. The present publication was written to fill this need.

Through careful selection and orderly presentation of information, it has been possible to include a broad range of subject matter not previously available within a single volume. Practical information is given on the properties, selection, and application of organic coatings, including methods of adequate surface preparation. Basic principles also are discussed. Thus, a description is given of the polymeric nature of the synthetic resins that are the basis for most of our modern coating systems, and relationships between polymer structure and properties are indicated. A unique feature which should prove useful to those concerned with the procurement or supply of organic coatings for the Government is a quick guide to Federal specifications for these materials in the form of a classified table and a series of summarizing charts.

Names and descriptions of some specific proprietary products are included for the convenience of the user. The omission of any particular product does not imply that it is considered unsuitable or unsatisfactory. Conversely, inclusion of a particular proprietary product does not constitute endorsement. Photographs of proprietary instrumentation and apparatus are included for illustrative and educational purposes and do not constitute approval or endorsement of the particular product. Use of the information given herein for advertising or publicity purposes is not authorized.

For the architect, engineer, maintenance superintendent, procurement officer, and others responsible for the proper selection and application of organic coating systems, this volume should be useful as a general manual, a unifying text, or a convenient source of authoritative information.

A. V. ASTIN, DIRECTOR.

Preface

Paints of the pigment-in-oil type have long provided man with durable protective and decorative coatings for his houses and other structures. Such paints, improved and embellished with new pigments in a wide variety of colors, are useful even today. In recent years, however, paralleling the tremendous growth of the plastics industry, conventional paints have given way more and more to new and often superior coatings based on the new synthetic resins and the new formulating techniques that have been developed. The list of available and useful film-forming materials is almost as long as the roster of different plastics, resins, and cellulose derivatives. These materials, singly or in physical admixture or chemical combination, have been modified with a wide variety of pigments, plasticizers, extenders, activators, stabilizers, solvents, and diluents to produce an almost endless proliferation of coating materials, each with its own set of useful properties. The information problem confronting those who must choose wisely from this bewildering array is indeed a formidable one.

It is a basic purpose of this publication to familiarize responsible personnel in the Federal establishment and elsewhere with the types of coating materials that are available, and to organize the essential information concerning such materials in a manner that will permit the selection and application of an adequate coating system for a particular job without requiring that the individuals responsible be or become expert coatings technologists.

The sheer magnitude of the problem precludes a discussion or even merely a listing of every material; nor would such an approach be desirable in anything but an encyclopedic treatment of the subject. Instead, the guiding philosophy throughout the preparation of this volume has been to anticipate and to meet the practical informational needs of the engineer, architect, maintenance superintendent, and coatings procurement officer—while keeping in mind the need for conciseness and clarity.

This volume is not intended to take the place of the many excellent manuals tailored in detail to the specific needs of a specialized Government agency or activity. Rather, it offers a broad survey of the field of organic coatings that will serve to orient the reader and may be useful in indicating areas in which available manuals might advantageously be modified to utilize the newer materials and techniques. The information has been selected and presented in a manner that will provide maximum usefulness when the monograph is used as an ajunct to the handbooks and manuals of particular agencies—to provide basic information and practical working details not usually found in the more specialized manuals.

It is hoped that this volume will contribute tangibly to the knowledge and perspective so essential for the wise choice and proper application of modern coating systems.

A. G. ROBERTS.

WASHINGTON, D.C.

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1. Introduction

1.1. Scope

Surfaces are painted to protect them from harmful agents in their environment, to decorate them, or to provide some functional purpose such as light diffusion or reflection, heat reflection or absorption, abrasion resistance, fire retardance, cleanliness, imperviousness, or identification. Whatever the objective of painting, it is successfully achieved only to the extent that the protective, decorative, or functional coating remains bonded to its substrate and retains its essential properties. To ensure this requires careful selection of the proper coating system, scrupulous attention to surface preparation, skilled application, and adequate maintenance. It is the purpose of this manual to provide sufficient information relating to these requirements to enable those responsible for the maintenance of structures and equipment to select the proper coating material for a particular application, and to provide those who must apply and maintain these coatings with sufficient detailed information to do the job in a manner that will ensure adequate adhesion and durability.

The subject matter is not limited to conventional paints but also includes pigmented and clear coatings based on a wide variety of cellulosic and resinous film-forming materials that have become available in recent years. The term "paint" is often used in its broadest sense to denote a liquid material that has the property, when applied in a thin layer, of hardening into a continuous film that adheres to the substrate; in this sense, any organic coating material may be considered a paint. A few inorganic coating materials, such as cement-water paints and phosphate coatings, also have been considered because of their important uses in the coatings field.

1.2. Basic Objectives and Arrangement of Information

This volume seeks to provide coverage in depth of the organic coatings field by giving basic principles and information as well as practical working details. Through treatment of both the fundamental and practical aspects of the subject, it is hoped that the volume will be found useful as a working manual, as a concise textbook, or as a convenient reference source on the properties, selection, and use of organic coatings.

It has been neither feasible nor desirable to specify a particular coating system for every application or to give individual instructions, without explanatory background, for handling every situation. Such a presentation, while appropriate and useful for specialized manuals of limited scope, would involve almost endless repetition of detail if applied to the entire field of organic coatings. Instead, the objective has been to provide an adequate basic understanding of the subject that would make repetition of detail unnecessary. Toward this end, each chapter deals with a major area of the coatings field. Cross references within the text show interrelationships among areas of information while serving to avoid repetition and conserve space. Specific references to Federal, Military, and other specifications are given at appropriate places, and an entire chapter has been devoted to a quick guide and summary of Federal specifications for organic coating materials. A consolidating chapter provides supplementary information and furnishes examples of use of the volume in solving typical coating problems.

With the wide variety of coating materials available today, the solution to a particular coatings problem is seldom a unique one. This publication has not presumed to make those decisions which are the prerogative of the

responsible agency or coatings official. Instead, it has sought to provide reliable and comprehensive information upon which such decisions might be based. By treating each broad aspect of coatings technology in one unified portion of the text, repetition of detail has been kept to a minimum and it has been possible to broaden the scope of information that could be included. Given such information in a well-indexed and accessible form the reader can readily extract the information he needs and arrange it himself in whatever sequence best suits his purpose.

In presenting information on the properties, selection, and use of organic coatings, the volume has endeavored to be a comprehensive guide rather than a specification. It should be understood, therefore, that *when the general or basic information presented herein differs from the stipulated requirements of a particular specification* or from the specific instructions of the manufacturer of a particular product, the requirements of the specification or the manufacturer's instructions normally should take precedence.

1.3. Structure and Use of the Index

The paramount objective of any index should be to lead the user quickly to *all* the information that pertains to his problem. Toward this end, entries have not merely been listed but have been organized under a system of headings and subheads that not only direct the user to the immediate subject matter but also make the index itself a source of integrated information that can lead him to pertinent related areas. To achieve adequacy of coverage and cross-referencing without undue repetition, a "pyramidal" arrangement of entries has been employed in which the user is directed to successively more detailed branches until the subject has been fully covered. Two examples will serve to illustrate how this arrangement provides maximum utility with minimal redundancy. It is suggested that the reader actually follow the examples through the index.

EXAMPLE 1: Suppose it is desired to obtain detailed information on *clear coatings*. One might first look for this under the general heading "Coatings", with the expectation of finding "clear" as one of the sub-entries under it. This is actually the way it appears in the index; reference is made to a single set of pages on clear coatings, with no further breakdown at this point (to subdivide the index further at this point would make the already long listing under "Coatings" very cumbersome, especially if such subdividing were applied generally to the other entries). The main heading, however, directs the user to "See also . . . under specific coating type", in this instance under "Clear coatings", where he finds a listing of the various types of clear coatings (drying oils, lacquer, varnish, etc.) as well as a general reference to their "durability compared to pigmented" types. Again, the user is directed to "See also under specific type" if he wishes further details; thus, he can look under "Drying oils" to find page references to types of drying oils such as boiled or raw oils, or to specific oils such as linseed or tung oil. Here, again, the user is told to "See . . . under specific oil" where he is given a final breakdown of detailed information; for example, under "Linseed oil" he will find references to its use in alkyd resins and in house paints, and he will learn (if he is not already

aware of it) that a water-soluble type of linseed oil is available; under "Tung oil" he will be directed to information on its use in spar varnishes, in wrinkle finishes, etc.

It is seen from the preceding example that even the user with only a general knowledge of clear coatings would be led by the index to all the relevant information in the text, through a series of expanding steps; and that he would learn about the basic types of clear coatings and of many specific materials along the way. Alternatively, the user with specific informational needs could enter the index at any stage in the interrelated chain of entries with equal success.

EXAMPLE 2: Let us consider briefly the general way in which the index deals with the complex and voluminous subject of *surface preparation*. In this case, it has been desirable and feasible to employ the "pyramidal" index structure largely under the main heading "Surface preparation for painting", and the bulk of the information on this subject is developed here. Major subheads provide references to general principles and methods and to each type of substrate (concrete, metals, wood, etc.), and these categories are further developed through detailed sub-entries. Cross references direct the user to "See also Surface pre-treatment, specific cleaning method, and specific substrate". The comprehensive listing under "Surface preparation" together with the cross references guide the user to all the pertinent information.

Attention is invited to the detailed treatment given to the subject "Coatings for" in the index. While neither the list nor the accompanying page references are exhaustive in nature, they provide an entree to places in the text which mention coating materials for many specific applications.

A formal *glossary* was considered beyond the scope of the present volume; however, the index will often serve in lieu of one to direct the user to places in the text where paint terms or concepts are defined or discussed.

Although practical considerations have necessarily limited the space that could be devoted to indexing, it may be apparent from the foregoing that the index is not a perfunctory one. The reader is urged to make full use of it.

1.4. Historical Background

1.4.1. Early History of Varnish and Paint

Varnish much like that which we know today was made by the Egyptians as early as 500 B.C. [1].[1] Some of it still endures today as a coating for their mummy cases. Their varnish was made of resin and oil and evidently was applied in a viscous, unthinned form with a blade or with the fingers. A durable varnish made by cooking amber resin with linseed oil is described in the works of Theophilus in the tenth century A.D. Theophilus ascribed his formulas to earlier compilations dating back to the eighth and the first centuries. His varnish formula remained the standard of the art for another 800 years. Turpentine, though known since early times, was used for other purposes (for example, as an embalming fluid) rather than as a varnish component or thinner until about the fourteenth or fifteenth century. The first technical treatise on the paint and varnish industry as it is known today was prepared by Watin in 1772. He described the formulation and manufacture of oleoresinous varnishes, spirit varnishes, and resin dispersions in turpentine. His book went through many editions with only minor changes and remained the standard of the varnish-making art until the turn of the twentieth century.

Paint in the form of finely divided solid particles (pigment) suspended in a fluid medium has been used since prehistoric times for decorative purposes. Protective and decorative paints using egg yolk or albumen, gum arabic, and beeswax as vehicles or binders were made for many centuries. Pigments often were suspended in water, with or without binder. For more durable paints, the pigment was suspended in a varnish vehicle like that described by Theophilus. Straight linseed oil paints, though slower drying than varnish-base paints, were lower in cost and easier to apply, and found considerable use during the middle centuries. During most of the nineteenth century, paints based on white lead-in-oil were widely used for both interior and exterior purposes.

For many centuries paint formulation was an art that was carefully guarded and handed down from one generation to the next. As the paints were made in small batches using crude grinding mills and laborious mixing methods, they were expensive and available only to the affluent segments of society. Not until the establishment of the first paint and varnish factories during the nineteenth century did paints begin to find their way into general use.

1.4.2. Twentieth-Century Developments

As with many of the arts of man, the paint and varnish industry, which had undergone little change for many centuries, felt the impact of the scientific and technological awakening ushered in with the twentieth century. New pigments, improved drying oils, cellulosics and synthetic resins, and a variety of modifying agents began to flow from research laboratories and production lines in ever-increasing numbers and became the basis for a never-ending stream of new coating materials.

A few milestones may be mentioned here. Titanium dioxide was developed as a superior white pigment with outstanding hiding power and durability. Tung oil, when heat-treated at 500 °F (260 °C), acquired excellent properties useful in the manufacture of fast-drying, durable paints and varnishes. Phenolic resins were developed and in combination with tung oil yielded varnishes of exceptional water resistance and outdoor durability. Linseed and soybean oil-modified alkyd resins were used in the manufacture of fast-drying paints with excellent gloss and weathering properties. The introduction of quick-drying nitrocellulose lacquers revolutionized the automobile and furniture finishing industries. Baked urea- and melamine-formaldehyde resins provided durable, gleaming finishes for automobiles, household appliances, and table tops. Recent years have seen the development of abrasion- and water-resistant vinyls, tough and chemically resistant epoxies, durable acrylics, heat-resistant silicones, hard high-gloss polyurethanes, and many others. The advent of water emulsion latex paints and convertible water-solution paints has added yet another dimension to the variety, usefulness, and complexity of the organic coatings field; the elimination of the hazards, inconvenience, and expense of organic solvents in such paints has given tremendous impetus to their further development.

Most of these new materials are discussed in the pages which follow. In the interests of an unencumbered and concise presentation, free use is made, throughout this publication, of common paint and technical terms, e.g., plasticizer, polymerization, copolymer, pigment volume concentration (PVC), extender, gloss, thermoplastic, emulsion, etc. The meaning of many of these terms is made clear through discussion at appropriate places in the text, and the Index will serve in lieu of a glossary to direct the reader to them. Standard definitions of many terms relating to paint, varnish, lacquer, and related materials are given in ASTM D16–59 [115].

[1] Figures in brackets indicate the literature references at the end of the text.
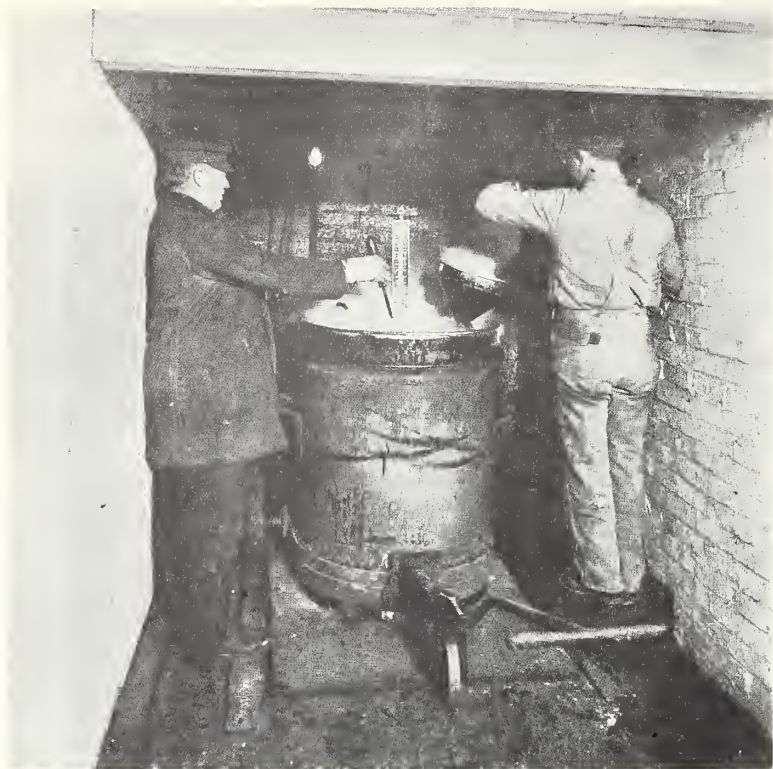
FIGURE 1.1. *Early varnish-making; putting in the oil.*
(Bottler, M., and A. H. Sabin, German and American varnish making, John Wiley & Sons, New York, N. Y. 10016, 1912.)
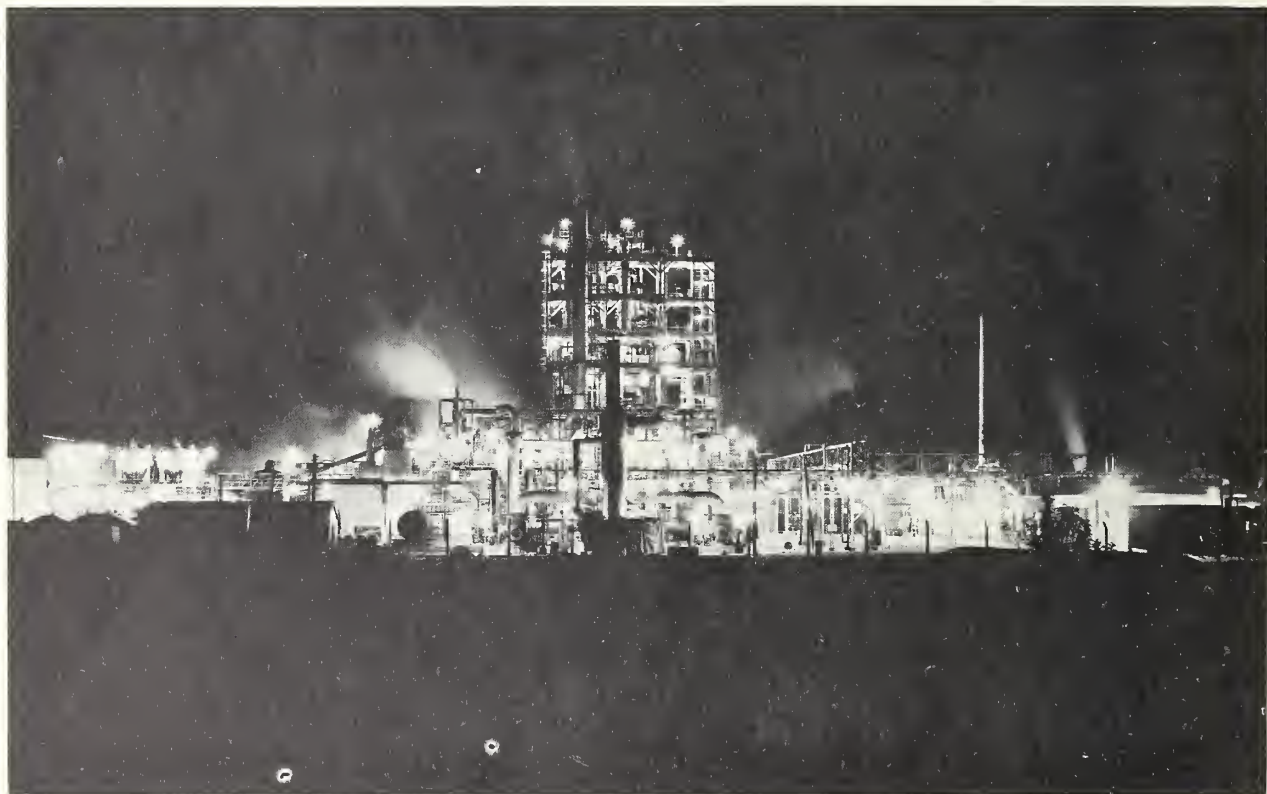
FIGURE 1.2. *Night view of modern phthalic anhydride plant.*
(Photo courtesy of Laporte Industries Limited, London.)

2. Types of Coatings

2.1. General Description and Basis for Classification

The fundamental constituent of all coating materials is the film-forming base which attaches itself to the substrate to which it is applied, and into which are incorporated all the other ingredients that impart to the film the special properties required for a particular purpose. In order to adhere to the substrate, the film must be applied in the form of a liquid that *wets* the substrate (see Chapter 6 on surface preparation) and then cures to a solid state. Some film-formers, such as linseed and other drying oils, are liquids of usable viscosity initially. Others, such as uncured phenolic or epoxy resins, are viscous liquids which may require thinning with suitable solvents and diluents before use. Many (e.g., cellulose derivatives) are solids in fibrous, granular, or powder form; these must be dissolved, dispersed, or suspended in a volatile liquid medium (vehicle) before they can be applied. Upon evaporation of the volatile portion, the solids are deposited in the form of a continuous, adherent, transparent or translucent film.

The film-forming base (often referred to as the *binder* in pigmented paints) need not be a simple or single resin. Often it is a copolymer (see sec. 3.1.4.2), such as polyvinyl chloride-acetate. Or the film-former may be a chemically reacted combination, such as a drying oil-alkyd. It may also be a physical mixture of two or more film-forming ingredients, such as an alkyd-nitrocellulose blend.

The film-forming solution constitutes a liquid vehicle in which insoluble pigment particles may be dispersed to give color, opacity, and increased outdoor durability to the film. Many other substances may be added to the vehicle (and if dissolved in it become a part of it) to achieve specific properties in the film—driers to hasten the film curing process, plasticizers to impart flexibility or moisture resistance or other properties, stabilizers to lessen the deteriorative effects of heat and sunlight, fillers and extenders to modify gloss, or improve mechanical properties or reduce cost, thinners (solvents, latent solvents, diluents) to adjust viscosity and to control the evaporation rate for proper application and flowout, etc.

The wide variety of coating materials that are available may be conveniently classified on the basis of their composition, behavior, and function, as discussed in the sections which follow.

2.2. Clear Coatings

2.2.1. Drying Oils

The drying oils used in organic coatings are derived chiefly from the nuts or seeds of certain plants and from certain species of fish. Chemically, these are mixed glycerides (glyceryl esters) of saturated and unsaturated fatty acids. They have the property, when exposed in a thin layer to the atmosphere, of "drying" or hardening into a clear or translucent film by a process of oxidation and polymerization (see sec. 3.1.1). An indication of their drying ability (chemical unsaturation) is given by their Iodine Number.[1] When combined with a hard resin, the drying oils impart their inherent flexibility, elasticity, and durability to the derived film.

The drying oils are useful in paints in both their raw and variously processed forms. RAW OILS, besides being the least expensive, possess the best brushability and the greatest penetrating ability; however, their flow and leveling properties are inferior to that of the processed forms. REFINED OILS have almost the same brushing and penetrating properties as the raw oils; however, because they have been purified by chemical and mechanical treatment, their clarity and color are improved and they can be heated to varnish-cooking temperatures without the formation of a sludge that would impair the drying properties and gloss of the varnish film. "BOILED" OILS are not actually boiled, but are drying oils which have been heated with lead, cobalt, and manganese compounds to produce a solution that will have the necessary drying properties; for practical purposes, the same drying results are achieved by adding soluble organic salts of these heavy metals to the cold untreated oil. HEAT-BODIED OILS are refined oils (usually alkali-refined) that have been held at an elevated temperature (about 500 to 600 °F [260 to 316 °C]) until sufficient polymerization has taken place to produce the desired viscosity. While such bodied oils lack the easy brushability and excellent penetrating ability of raw oil, they possess superior flow and leveling properties, convert to a dry film more rapidly, and yield films of higher gloss

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and paler color. BLOWN OILS are those through which air has been blown at temperatures around 200 °F (93 °C), resulting in partial oxidation of the oil with a consequent increase in its viscosity and in its tolerance for water. Blown oils are darker in color and less durable than the heat-bodied oils, but they have excellent flow, leveling, and gloss properties—in fact, they are so free-flowing that difficulties may arise from pigment settling in containers and from a tendency to run or sag when applied. Their brushability, penetrating properties, and drying rate resemble those of the heat-bodied oils.

2.2.1.1. LINSEED OIL, derived from the seed of the flax plant, is the most important and most widely used of the drying oils. In addition to being the only drying oil which is used extensively by itself as a paint vehicle (in exterior house paints), it is an important constituent of many high-grade varnishes and oleoresinous paints. In various combinations with alkyd resins (see sec. 3.4), it forms one of our most versatile and useful classes of coating material. Recently, a water-soluble from of linseed oil has been developed [121].

2.2.1.2. TUNG OIL is invaluable in imparting fast drying qualities, excellent water resistance, and exterior durability to varnishes. Its drying ability is the result of a highly unsaturated, conjugated double-bond molecular structure. Its tendency to form wrinkled films when used alone can be utilized in the manufacture of wrinkle finishes (see sec. 4.1.4.4).

2.2.1.3. DEHYDRATED CASTOR OIL somewhat resembles tung oil in its drying characteristics but forms a softer, more flexible film with some tendency (controllable) to develop after-tack. It has excellent color and color retention properties and is widely used in the paint and varnish industry.

2.2.1.4. PERILLA and OITICICA are important plant-derived oils with fast-drying properties. Oiticica oil has a conjugated double-bond type of unsaturation similar to that of tung oil.

2.2.1.5. REFINED FISH OILS have found extensive use in the low cost paint field and in the formulation of heat-resistant paints for such applications as smoke-stack exteriors, boiler fronts, and roofing, where their softness and elasticity can be used to advantage, and their tendency to yellow and to develop after-tack and undesirable odor is not objectionable. Current research on fish oils holds a promise of better utilization of these materials in the future.

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¹ For a description of Iodine Number and a discussion of its uses and limitations, refer to Federal Test Method 5061 of Fed. Std. No. 141 (see general bibliography).

2.2.1.6. SEMI-DRYING OILS are in a slower drying category than the oils just discussed. Typical of these are soybean oil, safflower oil, and tall oil (see sec. 2.2.1.8). Semi-drying oils dry to soft, tacky films at ordinary temperatures, but they may be blended or baked with faster-drying oils or hard resins to produce excellent coatings. When combined with a hard resin, the semi-drying oils, like the drying oils, impart their inherent flexibility, elasticity, and durability to the resultant film.

2.2.1.7. NON-DRYING VEGETABLE OILS, such as cottonseed, cocoanut, castor, corn, and peanut oil should not be confused with the drying and semi-drying oils. Although widely used in the organic coatings field, the non-drying oils function as plasticizers rather than as film-formers.

2.2.1.8. TALL OIL is a semi-drying oil derived, unlike the oils already described, as a by-product of the sulfate wood pulp process used in paper-making. Acidification of the black liquor skimmings from the pulping process yields an incompatible liquid mixture from which, upon separation, the tall oil is drawn off. The oil consists chiefly of a mixture of resin acids related to abietic acid, and of fatty acids related to oleic acid, together with a small proportion of nonacidic substances. Because of its ready availability, low cost, and good properties when combined with various resins, it is finding steadily increasing use in alkyd resin manufacture and in combination with other resins such as epoxies, phenolics, and styrenated resins (see Ch. 3).

2.2.2. Varnish

Although a varnish has sometimes been defined as any liquid composition which is converted to a transparent or translucent film after application as a thin layer, the term is most often used in a more specific and descriptive sense to denote a homogeneous mixture of resin, drying oil, drier, and solvent which dries by a combination of evaporation, oxidation, and polymerization to give a transparent or translucent film. The resin imparts certain desirable properties, such as hardness or faster drying, to the film. Such a varnish is often called an oleoresinous or oil varnish. It is made by cooking the drying oil and resin together until chemical combination and partial polymerization have taken place, and then adding the drier and solvent to the cooled ingredients. The ratio of oil to resin is customarily stated as the "oil length" (number of gallons of oil per hundred pounds of resin) of the varnish. Varnishes are further classified as "short oil" varnishes if their oil length is below 15 gallons, "medium oil" varnishes if their oil length is between 15 and 30 gallons, and "long

oil" varnishes if their oil length is over 30 gallons. Short oil varnishes dry more rapidly than long oil varnishes and form a harder film, but the long oil varnishes have greater elasticity and better exterior durability.

Interior varnishes often are based on linseed oil in combination with estergum or a maleic-modified rosin resin. Rosin-modified phenolic resins form varnishes with fairly good water and alkali resistance, but for exterior durability a long oil length is required. The most durable spar (wood) varnishes for exterior exposure are usually made from tung oil combined with a 100 percent phenolic resin (substituted phenol-formaldehyde, oil soluble—as described in section 3.3.2.1). The phenolics, as a group, yield varnishes of relatively dark color. Terpene-phenolic resins are lighter in color and lower in cost than the comparable phenolic resins; they have very good water and alkali resistance, but only fair exterior durability. The terpene resins themselves are low in cost and make good light-colored interior varnishes with good color retention and good water and alkali resistance.

Coumarone-indene resins are thermoplastic resins available in a wide range of hardnesses. Although poor in color and outdoor weathering, they contribute excellent water and alkali resistance and good dielectric properties to varnishes.

Petroleum hydrocarbon resins are soluble in drying oils and form varnishes with good water, alkali, and alcohol resistance, but only fair color.

Natural resins (sec. 3.17.2) such as congo, kauri, pontianak, and batu are often used in varnishes because of their low cost and their ability to impart specific properties such as hardness, gloss, and moisture resistance.

So-called alkyd varnishes differ somewhat from the conventional type of varnish in that the drying oil is co-reacted with the resin at the time the alkyd resin itself is being formed. Because of the wide versatility and importance of alkyd resin vehicles, these are discussed separately in section 3.4 on Alkyd Resins.

2.2.3. Spirit Varnish

A spirit varnish consists of a resin or gum (e.g., shellac or damar) dissolved in a volatile solvent (e.g., alcohol). Such a varnish dries primarily by evaporation rather than by oxidation or polymerization. A shellac varnish is covered by Fed. Spec. TT–S–300.

2.2.4. Lacquer

Much confusion has resulted from the diversity of meanings given to the term "lacquer." Some restrict the term to solutions of cellulose derivatives in volatile solvents, which dry by evaporation to form a solid film. Others, in a yet narrower sense, limit the term solely to solutions of nitrocellulose (plus modifying agents). Such restricted definitions ignore the existence of many modern coating materials which are, quite properly, called lacquers. For example, wide reference is made in the industry to vinyl lacquers, acrylic lacquers, butyrate lacquers, polyurethane lacquers, and others. (The long-known "Chinese lacquer" is a different type of material that dries slowly by absorption of oxygen in a cool, moist atmosphere. It is somewhat toxic even when dry and is little used in this country.)

The definition of a lacquer, to be generally acceptable and useful, should not exclude modern materials to which the term has been reasonably applied. Present usage strongly suggests that the properties most often associated with the term "lacquer" by those in the industry are: (1) rapid air-dry by solvent evaporation, (2) ease of application by spraying (although other means, such as brush or dip, are not necessarily excluded), (3) solubility of the dried film in the original solvents, making it relatively easy to touch up or repair. A lacquer may therefore be appropriately and usefully defined as a quick-drying, film-forming solution, especially well-suited for spray application, which dries by evaporation of its volatile constituents to form a coating that can be redissolved by the original solvents. (The latter requirement is met only by thermoplastic resins.)

Within the above definition, lacquers may be either clear or pigmented. In general, they are set to the touch (tack-free) within a few minutes after application, can be over-coated in about a half hour, and dry to a firm film in a few hours. The drying process can be considerably hastened, and adhesion and durability often improved, by baking the film at a moderate temperature.

Among the most widely used lacquers are those based on cellulose derivatives in combination with a modifying resin and a suitable plasticizer. The volatile solvent in which these film-forming ingredients are dissolved is a carefully balanced mixture formulated to give the proper application viscosity and drying characteristics. A discussion of the principles involved in formulating such a balanced solvent is given in the section on Use of Thinners (sec. 5.3.2).

2.2.5. Sealer

A sealer is a relatively thin liquid composition that is applied to porous surfaces to prevent excessive absorption ("suction") of the finish coats. Sealers for wood are essentially thinned versions of a varnish or a clear lacquer; their low viscosity and good affinity for

the substrate result in good penetration and sealing of the pores, so that good hold-out (uniform appearance) of topcoats is obtained. Sealers for plaster formerly were usually thin solutions of water-soluble substances such as starch or glue, sometimes containing a small amount of pigment to help seal the pores; such sealers are often referred to as "sizes." They are quite inferior to the oleoresinous and latex-base primer-sealers now available. (See sec. 2.3.5 on Latex Paints, and sec. 2.4.4 on Primers for Plaster and Wallboard.)

In the absence of a sealer on porous surfaces, the absorption of the finish coat often occurs unevenly, resulting in variations in the gloss, thickness, and durability of the topcoat. In the case of pigmented materials, the uneven absorption also causes variations in hiding power. In addition, the liquid vehicle may be selectively absorbed into the substrate, thus increasing the pigment volume concentration in the remaining topcoat material; this process reduces gloss and also may leave the pigment "starved" in binder and therefore prone to excessive chalking.

2.2.6. Wax Polishes

Wax polishes, although seldom used alone as a finish, are widely used to protect and give luster to other finishes for floors, furniture, automobiles, and appliances because of the relative ease with which they can be applied and renewed. Most wax polishes are mixtures of waxes of various degrees of hardness in a suitable solvent or dispersing agent, together with natural or synthetic resins and other ingredients to impart specific desirable properties. Hardness and luster are derived chiefly from the carnauba wax content (or other hard waxes such as candelilla, ouricury, esparto, or sugarcane). The semi-hard waxes (e.g., beeswax, parafin, montan, ceresin, and oxidized microcrystalline wax) contribute other properties, such as ease of application, flexibility, and lower cost. Shellac and other resins are often incorporated into wax floor polishes to reduce slippage, to increase gloss, or to increase durability. Colloidal silica also is effective in imparting anti-slip properties.

From the standpoint of proper selection and use, wax polishes are of three basic types: (1) The organic solvent type, in which the mixture of waxes is dissolved in a volatile medium such as a turpentine-mineral spirits mixture; this type may be in either paste or liquid form, depending on the amount of solvent present. (2) The aqueous emulsion type, in which the waxes are dispersed in water by use of an emulsifying agent such as morpholine or triethanolamine to produce a "self-polishing" liquid wax preparation. (3) An emulsion type in which the emulsified waxes are diluted with organic solvents, such as naptha, turpentine, or mineral spirits, so that the final liquid wax preparation contains both water and organic solvents.

The organic solvent type of wax polish, particularly in paste form, is generally considered to be the most durable and lustrous type, and the kind best suited for floors, although application is more difficult and considerable rubbing is required to bring out the full luster; this type cannot be used on asphalt tile or on *some* types of rubber tile, because these materials (especially asphalt) are attacked by the solvents usually employed. The water-emulsion type of wax preparation must be used on such surfaces. The water-plus-solvent type of wax emulsion finds application in furniture and automobile polishes and in emulsion polishes for vinyl tile and linoleum; the organic solvent helps to clean and brighten the surface and reduces the time required for drying to a tack-free state. Care should be taken that such solvent-containing emulsion types are not used on solvent-susceptible surfaces such as asphalt tile. Emulsion type waxes may incorporate a mild abrasive and possibly a soap or detergent to provide a cleansing action as well as a waxing operation. The abrasive should not be used in furniture polishes, but is useful in automobile polishes.

2.2.7. Strippable Coatings

Strippable coatings are coatings of low adhesion and considerable toughness designed to afford temporary protection against corrosion and abrasion of metal surfaces, parts, equipment, and structures. They are usually applied as a continuous envelope that is strong enough to remain intact and in place until the coating is slit and peeled off. Strippable coatings may be formulated for application by hot dip [133] or by spray [134]. The film-forming base is usually ethly cellulose, cellulose acetate butyrate, or a copolymer of vinyl chloride with vinyl acetate or vinylidene chloride (these resins are described in Chapter 3). In the hot-dip type, the film-forming base is dissolved in a hot plasticizer or oil into which the part to be coated is dipped; setting takes place as soon as the film cools. Spraying types are formulated with organic solvents in addition to plasticizers, and cure by evaporation of solvent. In both hot-dip and spray types, strippability is achieved by incorporating into the formulation a suitable proportion of an incompatible plasticizer or oil which will migrate to the coating-substrate interface to form a very thin liquid layer that prevents the development of coating-to-substrate adhesion.

Strippable coatings are used for the packaging and protection of items ranging from small tools and machine parts to large completely

assembled machines and equipment such as military aircraft, ship-board gun batteries, and field artillery pieces. Besides use for packaging a variety of small consumer articles (jewelry, kitchen gadgets, hardware, etc.), strippable coatings have become important to the industrial builder for the on-site protection of building hardware (ornamental railings, grilles, door knobs, and fixtures of brass, copper, and aluminum) during the period of construction.

Small articles are generally coated by the hot dip method. "Mothballing" of the large items is accomplished by first spraying a fibrous "cobweb" coating onto a framework of tape around the equipment to form a "cocoon", after which additional strippable coating material is sprayed on until a coating of sufficient thickness to provide the necessary strength and sealing properties has been built up. The "cocoon" coating is usually a polyvinyl chloride-acetate type of high vinyl chloride content, to which some polyvinylidene chloride has been added to promote cobwebbing. The final spray coating is generally a polyvinyl chloride-acetate type. The cocoon may be slit to permit flushing of the interior with dry air and the insertion of a desiccant or preservative, after which it is resealed. Major pieces of equipment may thus be stored for long periods, in readiness for immediate operation as soon as the cocoon is cut away.

2.2.8. Synthetic Resin Coatings

Among synthetic resin coatings, the distinctions between the various general types of coatings (i.e., whether a varnish, lacquer, enamel, etc.) and between clear and pigmented materials are secondary in importance to the nature of the resin or resins employed. The properties of the main classes of synthetic resins are therefore discussed separately in chapter 3.

2.3. Pigmented Coatings

Pigmented coating materials fall basically into two classes: (1) those based on clear solution-type vehicles, to which the pigment or blend of pigments has been added in the form of finely divided particles that are essentially insoluble in the vehicles, and (2) those consisting of a suspension of insoluble, finely divided pigment particles in a resin-water emulsion or latex (sec. 2.3.5.1). The latter type is of comparatively recent development, and many of the principles of formulation are quite different from those employed in conventional solution-type vehicles. Before detailed consideration of pigmented coating materials, a description of the pigments themselves is given.

2.3.1. Pigments

2.3.1.1. PIGMENT FUNCTION.—The pigment not only adds opacity and a decorative or functional color to the film but also increases its durability and protective character by screening out harmful light rays, controlling the transmission of moisture and gases through the film, imparting desirable mechanical properties, and contributing various other properties (e.g., corrosion inhibition, chalking, control of gloss), depending on the nature of the pigment and the concentration in which it is used.

The number of available pigments, particularly the colored ones, is very large, and it is not a purpose of this manual to list them all. However, a representative group of the most important types of pigments are described in the following sections. A list of Federal Specifications for pigments is given in the Index of Federal Specifications, Standards, and Handbooks [67]. A comprehensive list of the commercially available pigments appears in the Pigment Section of the Raw Materials Index of the National Paint Varnish and Lacquer Association [2].

A primary purpose of the pigment, in all pigmented coatings, is to hide the substrate by preventing the transmission of light through the film to the substrate (and out again). Colored pigments accomplish this, to a greater or lesser extent, by absorbing some of the light rays and reflecting others. White pigments, however, absorb relatively little light, so that their hiding power depends primarily on their ability to scatter and reflect the incident light. This in turn depends on the particle size and size distribution and on the difference in refractive index between the pigment and the surrounding medium. The higher the refractive index of the pigment, the greater is its hiding power, other factors such as particle size and shape being equal. The greatest hiding power among available pigments is exhibited by titanium dioxide; the rutile form has a refractive index of 2.76 as compared with an index of about 1.5 for the common paint vehicles.

2.3.1.2. WHITE HIDING PIGMENTS.—The number of white pigments having good hiding power is quite limited. The chief ones are basic carbonate white lead, basic silicate white lead, basic sulfate white lead, titanium dioxide (both anatase and rutile forms), zinc oxide,

leaded zinc oxide, zinc sulfide, antimony oxide, and lithopone. The latter is a co-precipitated mixture of zinc sulfide and barium sulfate.

The above pigments are often referred to as prime pigments. They are relatively high in cost and are most often used in combination with less expensive extender pigments.

White lead is a very durable pigment which contributes to the formation of flexible, durable films. It suffers, however, from a tendency to darken in industrial atmospheres. Although this tendency does not impair the protective character of the film, the decorative properties suffer. Titanium dioxide and zinc oxide are widely used in these environments to prolong the decorative life of exterior white paints.

Titanium dioxide is superior to white lead in hiding power, whiteness, and brilliance; the anatase form, because of its chalking tendency, imparts self-cleaning properties to white paints (not desirable in tints). Since the rutile form is chalk-resistant, the degree of chalking of titanium dioxide-pigmented paints can be controlled by the ratio of anatase to rutile pigment.

Zinc oxide contributes improved mildew resistance, increased durability, and other valuable properties to the paint film.

2.3.1.3. EXTENDER PIGMENTS are white pigments of relatively low refractive index approaching that of the common paint vehicles, so that they have little hiding power at ordinary pigment volume concentrations (below the critical PVC). However, they are very useful in combination with the prime pigments. Among the most important extender pigments are:

> hydrated aluminum silicates (china clays)
> magnesium silicate (talc)
> silica (usually in diatomaceous form, but sometimes as quartz)
> calcium carbonate (natural chalk and limestone ["whiting"], or chemically precipitated)
> barium sulfate (natural barytes or precipitated blanc fixe)
> calcium sulfate
> powdered mica

Although the extender pigments are low in cost, their use does not necessarily result in an inferior paint; in fact, the extenders usually contribute many valuable properties. They aid in producing the proper paint consistency for good non-settling characteristics and smooth application. They help to control the penetration of priming paints. They are useful for diluting colored pigments of great tinting strength. They assist in obtaining the desired surface appearance (degree of gloss or flatness) in the dried film. They may inhibit the tendency toward film cracking on aging, and they can improve various other mechanical properties of

the film (e.g., washability and abrasion resistance) through reinforcement of the film structure.

2.3.1.4. COLOR PIGMENTS comprise a wide variety of natural and synthetic materials, both organic and inorganic. They may conveniently be classified on the basis of their source and general nature as: (1) natural pigments, (2) synthetic inorganic pigments, or (3) synthetic organic pigments. Only the more important and widely used pigments in each class can be discussed here. From the standpoint of the paint user, the chief properties that govern the usefulness of a color pigment are:

> Color (hue, brightness, and saturation)
> Durability (lightfastness, heat resistance, chemical resistance—depending on the requirements of the application)
> Bleeding resistance (in oils and solvents)
> Tinting strength
> Hiding power (or, in some instances, transparency).

Properties which are primarily the concern of the paint manufacturer, such as ease of grinding and oil absorption, will not be considered here.

2.3.1.4.1. *Natural pigments* comprise the inorganic earth colors or mined products and a few organic materials of vegetable and animal origin. Of chief importance are the iron compounds, composed mainly of iron oxides in combination with siliceous material and smaller percentages of the oxides of manganese, aluminum, calcium, and/or magnesium, together with some carbonaceous matter. These ferroferric oxide pigments include the yellow ochers, the dark yellow siennas, the brown umbers, the red hematites and burnt siennas, and the black magnetite or magnetic oxide. With the exception of magnetite, which is 94–95 percent iron oxide (Fe_3O_4), the natural iron oxide pigments vary widely in composition. The yellow, brown, and red iron oxides are largely in the ferric form, and the ferric oxide (Fe_2O_3) content may range from as low as 11 percent in some of the ochers to as high as 80 percent in some of the hematites. The iron oxide pigments lack brilliancy, but they are widely used for their low cost, good durability, and excellent non-bleeding properties. However, the natural pigments, because of their variable composition, have been replaced in many applications by synthetic iron oxide pigments of greater uniformity, strength, and brilliance.

The natural organic color pigments are of only minor importance. Their chief use is in stains, artists' colors, and printing inks. In the vegetable group are Vandyke brown and various precipitated dyes. In the animal group are cochineal (carmine) and sepia.

2.3.1.4.2. *Synthetic inorganic pigments* of uniform composition and properties and in a variety of chemical types have largely replaced the natural pigments in modern paint technology. The most important types are discussed in the following paragraphs.

Synthetic iron oxide pigments of high purity are available as single oxides or blends of iron oxides in a range of colors that include yellow, orange, tan, red, maroon, brown, and black. The shade of the pure colors depends on the particle size and shape as well as on composition. Pure yellow iron oxide is hydrated ferric oxide ($Fe_2O_3 \cdot H_2O$) prepared by precipitation and oxidation from solutions of iron salts. Pure red iron oxide is ferric oxide (Fe_2O_3) obtained by calcining the hydrated form. Pure black iron oxide is a precipitated ferro-ferric oxide (Fe_3O_4) of bluish-black hue. The other iron oxide colors are made by blending yellow, red, and black forms. Venetian reds are calcium sulfate base iron oxide pigments containing from 25 to 40 percent of red iron oxide. The iron oxide pigments as a group are chemically inert, nonfading, bake-resistant, nonbleeding, and low in cost. They find wide use in applications where durability rather than brightness of color is required; for example, in paints for railway freight cars, in industrial paints, barn paints, floor paints, and metal protective paints.

Iron blues are complex ferric-ferrocyanides known by a variety of names. Chinese blue and Milori blue have a greenish tint tone (i.e., the tone perceived when the colored pigment is added in small quantities to a large quantity of light pigment); Prussian blue is reddish in tint tone. However, in mass tone (where the colored pigment predominates), Milori is reddish and Prussian is greenish. The iron blues are non-bleeding in oils and solvents but are somewhat reactive with certain organic vehicles. Although stable to acids, they have poor alkali resistance. They may be baked at 350 °F (177 °C). Their hiding power and tinting strength are excellent, as is their outdoor durability when used full shade. They are relatively low in cost and are very widely used in paints, lacquers, and enamels.

Chromate pigments comprise the chrome yellows and oranges, and molybdate chrome orange. Medium chrome yellow is almost pure normal lead chromate; the lighter shades contain lead sulfate. Blends of normal and basic lead chromate yield the chrome oranges, the higher proportions of basic lead chromate producing the deepest shades. Molybdate chrome orange is a coprecipitated mixture of lead chromate, lead sulfate, and lead molybdate; it is a strong, bright orange pigment with excellent hiding power. In general, the chromate pigments provide good hiding and durability at relatively low cost; however, the chrome yellows and molybdate orange are poor in alkali resistance while the chrome oranges have poor acid resistance. All except the deep chrome oranges tend to darken somewhat on exposure. All have excellent bleeding resistance. The deeper chrome oranges of high basic lead chromate content have been effectively utilized in metal protective primers. The chrome yellows enjoy wide general use in the coatings field.

Chrome greens are composite pigments consisting of an intimate blend of iron blue and chrome yellow. By varying the proportions of yellow and blue, a wide range of hues is obtainable. Chrome greens have high tinting strength and hiding power and very good color permanency and outdoor durability. Although sensitive to alkalis, they are resistant to acids and are quite stable on baking. Their cost is relatively low, and they find wide application in the coatings field.

Chromium oxides and their hydrates are green pigments of exceptional stability and color permanence. They are lower in tinting strength and hiding power than the chrome green pigments described above, but they resist acids and alkalis and withstand high temperatures. The pure chromium (chromic) oxide will withstand even ceramic heats. Chromium oxide pigment is relatively low in brightness; however, hydrated chromium oxide has good brightness. Their chief use is in applications where their stability to light, heat, and alkali justifies their higher cost.

Ultramarine blue is a dark, brilliant blue pigment with high decorative appeal. It is made by calcining mixtures of china clay, soda ash, silica, and sulfur in the presence of a reducing agent such as charcoal, pitch, or rosin. The calcined material is washed to remove soluble salts, wet-milled, filtered, dried, and ground into a range of particle sizes yielding different shades and tinting strengths. Although low in hiding power and tinting strength, ultramarine blue finds wide use as a tinting pigment in interior protective and decorative coatings, where it offers good heat stability, non-bleeding character, excellent resistance to most alkalis (except lime), and extreme lightfastness. It is very sensitive to acids, however, and since most vehicles develop some acidity during outdoor exposure, ultramarine blue is not usually used in exterior coatings.

Cadmium yellows and reds are essentially sulfides (yellow) or sulfo-selenides (red) of cadmium, usually combined with an inert base of barium sulfate. They are available in a wide range of colors, from a delicate light yellow to a deep maroon. They possess good color brightness, lightfastness, and resistance to acids. Their excellent alkali resistance makes them suitable for use in emulsion paints and special alkali-resistant finishes. Although

the yellows tend to fade and discolor on outdoor exposure, the reds and maroons exhibit good exterior durability. The cadmium pigments have excellent heat resistance and find important use in high temperature baking enamels.

2.3.1.4.3. *Synthetic organic pigments* comprise a very large and important group of colors that are prepared by the insolubilization or precipitation of organic dyestuffs. As with inorganic pigments, particle size and shape are important factors in determining the color shade obtained with a particular chemical type, the smaller particles generally producing the lighter shades and greater brightnesses. The most widely used synthetic organic pigments are discussed in the paragraphs which follow.

Copper phthalocyanine blues and greens are chemically inert pigments of high tinting strength and excellent lightfastness. They are highly resistant to acids and alkalis and are completely free from bleeding in oil and organic solvents, even at elevated temperatures. Although not in themselves readily wetted with water, they may be treated with surface active agents to render them easily dispersible for use in water base paints. Because of their strong, dark mass tone, the phthalocyanines are used chiefly in relatively light tints, yielding clean, bright blues and greens of outstanding durability. They have found wide acceptance in high quality paints, lacquers, and decorative enamels for exterior exposure. Phthalocyanine greens differ in composition from the blues in that most of the hydrogen atoms present in the blues have been replaced with chlorine atoms. The greens are free from the tendencies toward flocculation and crystallization exhibited by the blues; however, phthalocyanine blues with good resistance in these respects have been developed.

Toluidine reds are dyestuffs belonging to the insoluble azo group of pigments that are inherently insoluble in water without containing a metal precipitant. A range of light red to medium red shades is available. The toluidines have good hiding power and excellent brightness, durability, and color permanence when used full shade (undiluted), but the tints tend to fade. Although resistant to acids and alkalis, they bleed in many organic solvents, fats and oils. Toluidine reds find wide use in industrial and decorative enamels where brilliance of shade and durability are of prime importance.

Para reds also belong to the insoluable azo group. Though not as durable or lightfast as the toluidines, they are lower in cost. Their bright color and adequate lightfastness when used full shade make them useful in trim paints and in porch and deck paints. They are not suitable in tints because of fading.

Lithol reds are members of the soluble azo group of pigments. They range in shade from a light yellow red to a deep red, depending on the metal precipitant used to insolubilize them. By resination, maroon shades are obtained. The lithols show good resistance to bleeding in oils, hydrocarbons, and water, but they may bleed considerably in lacquer thinners, and their alkali resistance is poor. Although neither durable nor lightfast, they are the least expensive of the organic red pigments and find considerable use in interior applications where durability is unimportant and a strong color is desired.

Hansa yellows (toluidine yellows) are members of the insoluble azo group. Like the toluidine reds, they have good acid and alkali resistance but bleed in organic solvents and oils. They are durable and lightfast in full shade. Because of their alkali resistance, they are suitable for use in water emulsion paints, being superior to the chrome yellows in this respect. They are lower in cost than the cadmium yellows sometimes used in this application. A growing field of use for these pigments is in toy enamels where pigments free of toxic metals are required. Hansa yellows find wide use in paints, lacquers, and enamels requiring a durable, brilliant yellow pigment.

Benzidine yellows belong to the insoluble azo group. They are two to three times as strong tinctorially as the Hansa yellows but are somewhat less durable. They are more than ten times as strong as the chrome yellows. Like the toluidines, they have good acid and alkali resistance but bleed in lacquer solvents. They are of general usefulness in coatings where strong color and fairly good durability are required.

Tungstated and molybdated pigments are organo-metallic precipitates of the fugitive but brilliant basic dyestuffs such as malachite green, methyl violet, and the rhodamines. These pigments are strong and brilliant in color but are not sufficiently lightfast to withstand exterior exposure. They are fairly stable at moderate baking temperatures and fairly resistant to acids, but their resistance to alkalies is poor, and they bleed in lacquer solvents. Their chief use is in specialty coatings where permanence is unimportant and a striking decorative effect is desired. They are available in a variety of colors including blue, violet, green, yellow, and red.

Indanthrenes are strong, bright pigments possessing exceptional lightfastness even in light tints. They are non-bleeding in oils and solvents and resistant to acids and alkalis. Their use is limited by their high cost, so that they are used chiefly for toning and tinting other colors. However, indanthrene maroon has become a preferred pigment for high quality maroon automotive finishes. The blue also

finds use in the automotive field. Indanthrene greens and yellows are less used.

2.3.1.5. CORROSION-INHIBITING PIGMENTS.— A small but important group of pigments worthy of special mention are those used almost entirely for their ability to inhibit metallic corrosion. These include red lead (Pb_3O_4), sublimed blue lead (basic lead sulfate, blue), calcium plumbate, basic lead chromate, zinc chromate (zinc yellow), zinc tetroxychromate, and strontium chromate. Unique among the rust-inhibiting pigments is a recently marketed basic lead silico-chromate pigment consisting of a shell of basic lead chromate fused to an inert core of silica. The economy effected by limiting the costly basic lead chromate to the effective, outer reactive shell, together with the high bulking value of the light and inexpensive silica core, makes it feasible to incorporate a high volume concentration of this pigment into intermediate and finish coats as well as in primers, thus providing rust-inhibitive properties throughout the entire coating system.

The effectiveness of these corrosion-inhibiting pigments derives chiefly from their very limited solubility in water and their ability to chemically combine with the metal surface to produce an impervious, insulating film thus rendering the metal passive. When such pigments are incorporated in a metal priming paint, their limited solubility furnishes a small but adequate supply of corrosion-inhibiting ions without leaching enough pigment to render the film porous.

Zinc dust, when used in a primer in a sufficiently high concentration (92 to 95% of the dry film weight) to ensure particle-to-particle contact in the dry film, is an effective corrosion inhibitor for steel surfaces, producing the so-called "zinc-rich" paints [128]. It is now a generally accepted view [117, 118] that the zinc serves initially as the sacrificial (anodic) material in a galvanic reaction in which the steel, as cathode, is afforded protection at the expense of the zinc. The period of cathodic protection is limited by the build-up of zinc corrosion products at the metal-coating interface, which stifles the galvanic action; however, the deposited corrosion products form a hard, impervious, adherent barrier layer that is combined with both the coating and the substrate and affords excellent long-term protection against corrosion.

The formulation of metal primers incorporating corrosion-inhibiting pigments is discussed in section 2.4.2. Important principles and precautions which should be borne in mind when applying corrosion-inhibiting primers are discussed in section 7.2.3.

2.3.1.6. METALLIC PIGMENTS for use in paints are, with the exception of zinc dust, usually in flake form. The flakes are obtained by rolling out the metal particles in a ball mill or by hammering thin sheets of the metal in a stamp mill, in either case in the presence of a lubricant. They are either leafing or non-leafing, depending on whether or not they have been coated with a leafing agent (usually stearic acid) and polished during the manufacturing process. In a suitable vehicle, the flakes coated with leafing agent float to the surface of the paint, where they orient and interleave to form an almost continuous, bright metallic surface that is highly resistant to the passage of moisture and gasses, high in hiding power and specular light reflectance, and durable on exterior exposure. The coarse particle sizes produce the brightest, most highly reflective surfaces, while the fine particles are preferred in decorative coatings, printing inks, and aerosol paints.

In the non-leafing type, the metal flakes, instead of floating to the surface and forming an interleaved layer, remain suspended throughout the film. Although a high degree of reflectance is not possible with this type, a wide array of different colored metallic shades (including hammertone finishes) can be achieved, depending on the particle size and size distribution. The larger particles produce the greatest brightness or sparkle, while the fine particles yield the highest opacity and deepest shades.

2.3.1.6.1. *Aluminum* is the most widely used metallic pigment. It is available both as a powder and as a paste, in a variety of grades according to particle size. Aluminum paints are lightfast, heat-resistant, water-resistant, and durable on outdoor exposure except in acidic or alkaline environments. The leafing types are high in hiding power and in moisture resistance and provide an effective barrier against the transmission of water vapor and gases through the film. Important applications for aluminum paints include marine coatings, aircraft coatings, solvent tanks, transmission line towers, highway bridges, furnace fronts, and interior decorative finishes.

2.3.1.6.2. *Metallic copper and its alloys* with aluminum, tin or zinc yield the popular bronze finishes that range in shade from a light brass to a dark antique copper, depending on composition and on the heat treatment received during manufacture. Care in formulation is required to counteract the tendency of the copper bronze pigments to retard the drying of oil, varnish, and other vehicles that cure by an oxidative process. These pigments are high in hiding power but tend to discolor on exterior exposure. They are used chiefly in interior decorative finishes, specialty lacquers, printing inks, and anti-fouling paints. The latter often are made with a dendritic, non-leafing type of copper pigment.

2.3.1.6.3. *Zinc dust* is made by distilling zinc and condensing it under conditions that prevent coalescence. It has very high hiding power, being almost completely opaque. It is used chiefly in corrosion-inhibiting paints for steel, where it serves initially as the sacrificial anodic material providing cathodic protection to the steel substrate and later as a protective barrier (see sec. 2.3.1.5). It is used also in paints for galvanized surfaces, where it provides good adhesion. It is not resistant to acids or alkalis.

2.3.1.6.4. *Gold and silver flake* are used principally in decorative applications such as sign writing, book-binding, picture frames, and glass and chinaware.

2.3.1.6.5. *Stainless steel flake* has recently been used as the main pigment, along with some organic pigment, in a metal protective paint reported [3] to have shown excellent durability in corrosive exterior environments. The effectiveness of the stainless steel pigment is attributed not to rust-inhibitive properties but to its own chemical resistance plus its exceptional resistance to moisture. The aged film takes on the appearance of stainless steel itself.

2.3.1.6.6. *Other metallic pigments* used to a limited extent in the coatings field are nickel, tin, and lead.

2.3.1.7. BLACK PIGMENTS comprise the synthetic carbons manufactured by various fume and incomplete combustion processes, natural and synthetic graphite, pyrolyzed vegetable and animal blacks, and the naturally occurring combinations of carbonaceous and siliceous materials known as mineral black. Black iron oxide has already been discussed under Color Pigments (sec. 2.3.4).

Carbon black (sometimes called channel black) is manufactured by the closely-controlled burning of natural gas. It is the finest of the black pigments, the particles being of colloidal dimensions. It is the blackest of pigments and the highest in tinting strength and opacity, and it finds wide use in the coatings field. Other synthetic blacks are lampblack, furnace black, and thermal black. *Graphite* is a soft crystalline form of carbon that occurs in natural deposits of varying carbon content; it can also be manufactured by heating coke or charcoal with about three percent of iron in the high temperature of an electric furnace. Compared with other black pigments, graphite is relatively low in blackness and tinting strength and is used chiefly for its protective qualities and its electrical conductivity. The various synthetic blacks (carbon black, lampblack, etc.), although differing in amount of fixed carbon, particle size, oil absorption, and

tinting strength, are all stable to light, heat, acid, alkali, and atmospheric conditions.

Vegetable blacks may contain from 50 to 90 percent of fixed carbon, depending on the vegetable material from which they are made. *Animal blacks* (boneblack) contain only 10 to 20 percent of carbon, the remainder being chiefly calcium phosphate. Although they are much lower in tinting strength than the carbon blacks, they also have a much lower oil-absorption, so that larger proportions can be incorporated into a formulation to produce low sheen black finishes. Boneblacks also find use in artists colors and in latex paints. *Mineral blacks* are sometimes used in place of boneblack but are more variable in composition and properties. Mineral and vegetable blacks are used mostly to color cement and mortar.

2.3.1.8. FLUORESCENT PIGMENTS are finding increasing use in high visibility paints. Although formerly too expensive and short-lived for practical use, specially formulated fluorescent paints are now available that will retain satisfactory color and fluorescent properties during a year or more of exterior service in temperate climates. Fluorescent substances have the property of absorbing energy in one spectral region and re-emitting it in another spectral region of lower energy (longer wavelength). A number of organic and metal-organic dyes yielding a variety of fluorescent colors are available. For high visibility aircraft paints [4, 4a], a red-orange fluorescent pigment has been preferred because this color affords high contrast with outdoor surroundings and is in the spectral region to which the eye is quite sensitive. This pigment absorbs energy in the ultraviolet and blue regions and re-emits it in the red-orange region. The re-emitted light is added to the light ordinarily reflected from the paint surface, greatly increasing its brilliance. The total light radiated and reflected from a fluorescent paint may be three to four times as great as that of the same color without the fluorescence.

So-called "daylight" fluorescent paints utilize chiefly the visible, blue portion of the spectrum to produce fluorescence, the harmful invisible or "black" ultraviolet (which would soon deteriorate the fluorescent pigment) being largely screened out by the use of an ultraviolet absorber or inhibitor in the paint formulation. The initial reduction in brightness from not utilizing the ultraviolet is offset by a substantial gain in exterior durability.

Fluorescent pigments are low in opacity. The fluorescent paints made from them, to be fully effective, must be applied over a white undercoat that will reflect the light which would otherwise be transmitted through the coating and lost by absorption into the substrate [139].

The use of high visibility, daylight fluorescent paints on some aircraft is believed to have significantly lessened the risk of mid-air collisions. Other applications include warning signs for hazardous areas or equipment, explosives- and fuel-carrying vehicles, advertising signs, and eye-catching decorative effects both indoors and out, in artificial light as well as daylight.

2.3.2. Oil Paints

Oil paints consist basically of pigment particles dispersed in a drying oil or varnish vehicle, together with thinners to provide a suitable consistency and evaporation rate for proper application, and driers to give the desired curing characteristics. Oil paints dry by a combination of solvent evaporation, oxidation, and polymerization. The several types of oil paints may be distinguished as follows:

2.3.2.1. STRAIGHT OIL PAINTS are those utilizing a drying oil or combination of drying oils as the nonvolatile vehicle. Of the various drying oils available (see sec. 2.2.1), linseed oil is by far the most widely used because of its excellent brushing characteristics, wetting and penetrating properties, adhesion, elasticity, and durability on exterior exposure, as well as its general availability and relatively low cost. The linseed oil film is fairly permeable to water vapor—a property that is useful for reducing the tendency toward blister formation in paints on wood and other porous surfaces, but one which limits its usefulnes in applications where low permeability and good chemical resistance are required (e.g., an industrial metal paint). Oil paints are relatively poor in abrasion resistance, in resistance to water immersion, and in resistance to corrosive (especially alkaline) environments.

Both raw and bodied (heat polymerized) linseed oil are used in paints. The raw oil, because of its superior wetting ability, is used extensively in metal primers; the bodied oil is used in finish coats because of its faster drying and better leveling characteristics. High-quality exterior house paints are still based largely on the time-tested linseed oil vehicle. Pigmentation consists of various combinations of titanium with lead and/or zinc pigments and extender pigments.

2.3.2.2. OLEORESINOUS PAINTS consist of a dispersion of pigment particles in a varnish or oleoresinous vehicle, i.e., a vehicle in which the drying oil and resin have been combined by a cooking process. The addition of the resin reduces the permeability and increases the chemical resistance and hardness of the film as compared to a straight oil paint. The resin, depending on the choice, may also contribute other desirable properties, such as faster drying, increased gloss, improved adhesion, and greater durability. The types of resins employed have been discussed in sec. 2.2.2 on Varnish. Of particular importance are oleoresinous paints ultilizing phenolic resins and alkyd resins.

Phenolic paints based on an oil-soluble phenolic resin (section 3.3.2.1) combined with tung oil have very good water resistance and weathering resistance. Their fast drying and poor wetting characteristics, however, necessitate very thorough surface preparation to obtain adequate adhesion. Since phenolic paints continue to cure and harden on aging, failure from a lack of intercoat adhesion can occur if too much time elapses between coats. Ordinarily, successive coats of phenolic paint should be applied within 24 hours after the preceding coat. This time may be extended somewhat provided a small amount of a strong active solvent is added to the follow-up coat.

Alkyd paints are among the most versatile and useful materials in the entire field of organic coatings. The oil-alkyd vehicle on which such paints are based can be varied over a wide compositional range to give a broad range of coating properties for numerous applications in the consumer, manufacturing, and industrial maintenance fields. Among the valuable properties imparted to paints by alkyd resins are fast dry, hardness, and durability, with excellent chalk resistance, gloss, and color retention. A comprehensive discussion of alkyd resins is given in section 3.4.

Long-oil alkyds of the air-drying type are widely used in high quality interior architectural paints and enamels. The long-oil alkyds are also the basis for durable exterior trim enamels for both wood and metal surfaces. Blister and stain resistant exterior house paints based on long-oil alkyds plus added bodied oil are available but have not yet achieved wide use. Medium-oil alkyds are found in many good quality floor, porch and deck enamels. Baking-type medium- and short-oil alkyds, often in combination with urea- or melamine-formaldehyde resins, are the basis for premium coating materials of exceptional durability that find wide use in automotive enamels, appliance finishes, and industrial equipment coatings. The uses of alkyd resins are discussed in greater detail in section 3.4.1.3.

2.3.3. Pigmented Lacquers

By dispersing suitable pigments in a lacquer vehicle, opaque and colored lacquer-type paints are obtained which possess the characteristic sprayability, fast dry, and repairability of clear lacquers as described in section 2.2.4. Since the solids content of lacquer formulations is limited by the viscosity and solubility of the film-forming base in the volatile solvent medium,

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it is necessary to use prime pigments with maximum hiding power and low oil absorption to achieve good hiding without an undue increase in consistency. Extender pigments are not used in lacquers, since they increase consistency and reduce the proportion of film-forming base that can be used, without contributing to hiding power.

One of the first and most important pigmented lacquers was based on nitrocellulose plasticized with camphor or castor oil. Later, the combination of nitrocellulose with an alkyd resin and suitable pigments and plasticizers yielded the widely used "Duco"-type automotive finish. After many years nitrocellulose-alkyd combinations are still the basis for many of our present-day lacquers. Other film-forming materials used in the formulation of pigmented lacquers are cellulose acetate, cellulose acetate butyrate, ethyl cellulose, vinyl resins, and polyurethanes—to name only a few. Very recently, acrylic lacquers having excellent hardness, durability, and gloss have been developed and are being widely used in the automotive finishing industry. The properties of many of the resins used in lacquers are given in chapter 3 on Properties of Synthetic Resins for Coatings.

2.3.4. Enamels

Enamels are pigmented coating compositions that yield films characterized by smoothness and freedom from brush or other tool marks. Although most enamels are glossy, flat enamels also are available. Enamels are usually thought of as hard coatings. They are often of the baking type, as in the case of automobile and appliance finishes in which a short-oil alkyd is combined with a melamine or urea resin to produce a hard, durable finish. Floor, porch, and deck enamels are air-drying types that are often based on a medium-oil alkyd resin. Exterior architectural enamels are usually based on long-oil alkyd resins modified with drying oils such as linseed, soya, or dehydrated castor. Pigmented varnishes often fall into the enamel classification. Rutile type titanium pigments are preferred in exterior enamels because of their excellent hiding power and resistance to chalking. The pigment volume concentration (ratio of pigment to binder) of enamels, though dependent on the nature of the pigments and extenders employed, is generally lower than that of ordinary paints (see sec. 4.1.4.4).

2.3.5. Latex Paints

2.3.5.1. The various types of pigmented coatings that have been discussed thus far, whether oil paint or lacquer or enamel, have consisted basically of insoluble pigment particles dispersed in a homogeneous liquid vehicle consisting primarily of drying oil or resin solution. In these coatings the film-forming ingredient has been dissolved in organic solvents to give a vehicle having a single, continuous solution phase. In latex paints, however, the structure of the system is very different. The resinous or film-forming ingredient,[1] instead of being dissolved in a solvent medium, is dispersed (in the presence of an emulsifying agent) in the form of fine particles in a liquid (water) which is not a solvent for the resin. The pigment, also, is suspended in the water medium.

The use of water as the volatile vehicle in latex paints offers many advantages. It is readily available, inexpensive, noncombustible, nontoxic, odorless, and colorless. Storage facilities for a variety of organic solvents are not needed. Its evaporation rate is well suited for brush or roller application. The paint may be applied on damp surfaces or in damp weather and is not harmed by rain an hour or two after application. Surfaces may usually be recoated the same day, or under favorable conditions after an hour or two of drying. Brushes, rollers and containers can be cleaned by washing in warm, soapy water after completion of the work.

The disadvantages of water as the volatile vehicle stem from: its high surface tension which may cause foaming, crawling, or cratering of the applied film; its high heat of vaporization which slows evaporation and lengthens the flash-off time necessary to avoid blistering in baked coatings; its essentially fixed boiling point which makes it difficult to adjust evaporation rate in the manner that is possible with mixtures of organic solvents; and its susceptibility to freezing under adverse storage or application conditions.

2.3.5.2. FORERUNNERS of our modern latex paint vehicles were the alkyd resin emulsions that first appeared around 1929, some twenty years before the advent of commercial latex paints. The vehicles of these early resin emulsion paints consisted of a dispersion of a long-oil alkyd resin in water in the presence of considerable amounts of casein and other emulsifying agents. Paints made from these vehicles had a number of faults, including poor emulsion stability, clogging of paint brushes, poor water resistance, and a general lack of the outstanding properties usually associated with alkyd resins. Subsequent developmental work greatly improved the properties of alkyd resin emulsions, and their usefulness for interior paints was recognized in 1940 by a Federal Specification (TT–P–88). This was followed in 1947 by a Federal Specification (TT–P–18) for an exterior masonry paint based on an

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[1] Contrary to a popular misconception, a latex paint does not necessarily or even usually contain rubber, as will be apparent from the discussion of types of latex paints given in subsection 2.3.5.6.

alkyd resin emulsion. Alkyd emulsion paints are supplied in the form of a paste that is thinned with water before use. Since the long-oil alkyds on which they are based are liquid resins that have been only partly polymerized during manufacture, the paint film laid down must harden by a process of oxidation and polymerization after the water phase has evaporated, in the same manner as when deposited from an organic solvent solution. With the introduction of latex paints in 1949 and their subsequent wide acceptance, interest in resin emulsion paints dwindled. Today, alkyd resin emulsions find their chief use in blends with the latexes.

Actually, a latex paint is also a resin emulsion paint; however, it is a special type that is characterized by the higher molecular weight, smaller particle size, and more uniform size distribution of the resin particles as compared to the older, so-called resin emulsion paints. These properties of the latex are achieved by an emulsion polymerization process (sec. 3.1.3.3) which not only permits better control of the polymerization than is possible by bulk or solution methods but also permits the development of a high molecular weight polymer without problems of high viscosity or insolubility.

2.3.5.3. USES.—Latex paints are particularly well-suited for use on porous, absorbent surfaces such as plaster and masonry. The latex particles, although very small, are still large compared to the size of a dispersed polymer molecule in solution; hence, they do not penetrate into porous surfaces to so great an extent as do solution-type coatings, and their sealing properties are excellent. The inherent, good sealing properties of the latexes are utilized to the maximum in the formulation of primer-sealers (see sec. 2.4.4). Although latex paints may be successfully applied in most instances without requiring a primer-sealer, use of the latter provides maximum holdout of topcoats and is particularly useful in securing uniform gloss, hiding, and color over substrates (especially plaster) of uneven porosity or composition.

Latex paints are not alkali-sensitive and may be applied even over unaged (but not fresh, uncured) masonry or plaster surfaces. It should be noted, however, that when latex paints are modified with other materials (e.g., an alkyd resin) to achieve some of the advantageous properties of the modifier, the alkali resistance of the latex may be impaired. Also, the same non-penetration properties of the latexes which give them their excellent sealing properties causes difficulties when they are applied over chalky surfaces, because of their inability to penetrate the chalk to adhere to the substrate.

The water demand of masonry surfaces must be met either by diluting the paint with water or, more desirably, by dampening the surface to be painted. Excessive dilution of the paint itself will break the emulsion.

Although the widest and most effective use of latex paints has been for interior coatings on plaster and wall-board, and for exterior masonry surfaces such as brick, cinder block, stucco, cement, and weathered asbestos shingle, some latex paints have been formulated for use as exterior house paints on wood, as metal primers, and as industrial alkali-resistant coatings. Most latex paints give a flat or matte finish; however, acceptable gloss and semi-gloss types have been developed. Industrial baking-type latex finishes are also under development. More specific information concerning uses of latex paints is given later in this section in the discussion of the individual chemical types of latexes that are available.

2.3.5.4. FORMULATION.—The film-forming resin on which latex paints are based is a long-chain polymer of high molecular weight that has been produced, by an emulsion polymerization process (section 3.1.3.3), in the form of very small spherical particles (not over 0.2 micron nor below 0.01 micron in diameter). Even a small proportion of large particles will act as seeds to accelerate coagulation of the smaller ones. The emulsified or dispersed state is achieved by surrounding each resin particle with a film of emulsifying agent. Dispersion of the resin particles in the water vehicle constitutes an oil-in-water type emulsion, which is most stable when both phases are present in about equal proportions. Excessive thinning with water breaks the emulsion by reducing the thickness of the emulsifying film around each particle. At high solids content (about 70 percent), the emulsion inverts to the water-in-oil type and is no longer thinnable with water.

Latex emulsions differ from resin solutions in a number of important respects. In vehicles of the resin solution type, the solids content is limited by the viscosity and the solubility of the resin in the solvents employed. These properties in turn depend on the molecular weight of the resin, the viscosity increasing and the solubility decreasing with increasing molecular weight. Although durability and mechanical properties generally improve with increasing molecular weight (increasing polymer chain length), a practical upper limit is imposed by the necessity for maintaining a practical viscosity and solubility. Latex emulsions do not suffer from these limitations. Since the latex particles are suspended, not dissolved, in the water phase, insolubility at high molecular weights is a desirable property rather than a problem. Moreover, since the latex particles are not dissolved in the water, they contribute

little to the viscosity of the vehicle. Thus latex paints are able to utilize the inherent advantages of high molecular weight and high solids content without the viscosity and solubility limitations imposed upon solution-type vehicles.

The formulation of latex paints, however, involves characteristic problems of its own. Before a pigment is incorporated into the resin emulsion, the pigment must itself be dispersed in water in the presence of an efficient dispersing agent. Titanium dioxide, particularly the rutile form, is the preferred white hiding pigment. Extender pigments (e.g., calcium carbonate, china clay, mica, etc.) are used to help control flow, leveling, film build, and gloss; extenders may also have a pronounced effect on film properties such as cleanability, scrub resistance and appearance. Good dispersion is essential for high solids content, package stability, freeze-thaw resistance, good flow and leveling with minimum floating and flooding, and for maximum hiding power and color uniformity. Thickeners, in the form of water-soluble protective colloids such as casein or methyl cellulose, are often necessary to stabilize the emulsion and to produce a suitable consistency for good application properties. These water-soluble colloids are used in minimal amounts (or not at all) in exterior formulations because they tend to reduce the water resistance of the film in which they remain. Bacterial contamination during manufacture must be guarded against, and a preservative (e.g., one percent of a phenyl mercuric salt) must be incorporated to inhibit the growth of bacteria, mildew and mold in the container and in the film. An anti-foaming agent must be present to suppress the tendency toward foaming during manufacture, filling of containers, and application. The pH of the system is an important factor in stability. Styrene-butadiene and acrylic latexes must be maintained on the alkaline side; for best results, a pH range of 9.0–9.5 is usually maintained. Polyvinyl acetate latexes are slightly acidic. Finally, when the paint is applied to a surface, the individual resin particles must somehow fuse to form a continuous film upon evaporation of the water vehicle.

2.3.5.5. FILM FORMATION results from coalescence of the latex particles under the influence of driving forces generated when the resin particles are brought into close contact as the water evaporates. As the last portions of water are vaporized, capillary forces act strongly to deform the latex (polymer) spheres, thus filling the voids left by the vacating water, so that fusion of the particles takes place and a continuous film is formed. If the polymer is too rigid to deform sufficiently under the forces generated, then coalescence does not occur and

a spongy or powdery structure rather than a continuous film remains after evaporation of the water.

The polymer deformability upon which film formation depends has its basis in the physicochemical structure of the polymer that determines the modulus of elasticity and the glass transition temperature, T_g. At temperatures above T_g, a rigid polymer acquires rubber-like characteristics which permit it to deform appreciably under relatively low stresses. The temperature at which a latex paint is applied is therefore the most important environmental factor involved in film formation. Application at low temperatures (below 50 °F or 10 °C) should be avoided, since drying and coalescence suffer. Porous surfaces require higher temperatures for film formation than non-porous surfaces. Film formation is also influenced by the size and the size distribution of the latex particles, the quality of the dispersion (freedom from flocculation), the pigment volume concentration, and the presence of coalescing aids. A small quantity of coalescing agent, in the form of a high-boiling solvent or plasticizer that acts to soften the polymer spheres during the final stages of drying, is sometimes incorporated as an aid in film formation. The time required for film formation depends on the rate of water removal as determined by the temperature, the relative humidity, the porosity (water demand) of the substrate, and the film thickness. The final latex film, while continuous and water-resistant, remains permeable to water vapor (i.e., it "breathes") and therefore does not tend to blister when applied over damp surfaces.

2.3.5.6. CHEMICAL TYPES.—Three different types of latex paints, based on the general chemical nature of the polymer employed, are presently in wide use. These are: (1) the styrene-butadiene type, (2) the polyvinyl acetate type, and (3) the acrylic type. The most important properties of each type are briefly considered below.

2.3.5.6.1. *Styrene-butadiene* latex was the first commercially available type, is the lowest in cost, and has the largest market. The chemical unsaturation imparted by the butadiene portion of the copolymer allows initial use of a soft yet strong film-former to obtain maximum pigment binding and film continuity, while laying down a film which subsequently hardens rapidly (through a curing process similar to that which takes place in oleoresinous paints) to a tough, durable coating. However, this reactivity also results in yellowing and eventual embrittlement on aging. Protective colloids such as methyl cellulose and casein, despite their adverse effect on water resistance, are usually necessary in styrene-butadiene la-

texes to stabilize the emulsion. The latex is compatible with a wide range of long-oil alkyds, heat-bodied drying oils, and long-oil varnishes. It may be blended with these (after first emulsifying the modifier) to obtain a wide variety of end-use properties. Rutile titanium dioxide is the preferred pigment for maximum hiding and good non-chalking properties.

Styrene-butadiene latexes have found wide application in flat and low sheen interior paints, exterior masonry paints [5], high-solids texture paints, and in primer-sealers. The somewhat objectionable odor of the wet film disappears soon after drying. Specialized uses include coating the interiors of tank cars carrying hot caustic soda, the dip-coating of mattress springs, and as a baking-type primer for automobiles. Industrial gloss and semi-gloss paints have been developed which are suggested for use on metal furniture, automobile interiors, drums, and motor shells. One of the latest developments in styrene-butadiene latexes is an industrial type primer in which the residual chemical unsaturation is utilized to effect further polymerization *in situ* through the use of catalysts and heat to produce a hard, solvent-resistant film having improved adhesion to metal and excellent salt spray resistance. Suggested end uses for this primer include automotive parts and bodies, metal furniture, electrical equipment, refrigerators, and airconditioners.

2.3.5.6.2. *Polyvinyl acetate* (PVA) latexes are intermediate in cost and usage among the three main types of latex. Polyvinyl acetate itself is usually plasticized in order to yield a film having adequate flexibility. For this purpose it may be internally plasticized (pre-plasticized) by copolymerization with a suitable monomer, or it may be externally plasticized (post-plasticized) by blending with 10–15 percent of a chemical plasticizer such as dibutyl phthalate or a polymeric plasticizer such as an alkyd resin. Maximum durability is obtained either by pre-plasticizing or by the use of polymeric plasticizers that remain in the film throughout its life. The chemical plasticizers gradually volatilize, and their loss eventually results in embrittlement of the film.

PVA emulsions are slightly acidic and may cause corrosion of unprotected metallic containers with resultant impairment of emulsion stability by the metallic ions liberated.

PVA latexes have excellent sealing properties and find wide use in primer-sealers. They have performed well in interior finishes and have found use also in exterior coatings [6] for masonry, asbestos shingle, and wood such as yellow pine and red cedar. The PVA film has a relatively high permeability to water vapor that permits "breathing" and hence

minimizes blistering. Like other types of latex, it does not penetrate chalky surfaces sufficiently to provide a good bond to the substrate. Although PVA formulations said to adhere to chalky surfaces have been offered recently, not enough experience with these is available at this writing to reliably assess their effectiveness. In addition to the usual flat finishes, PVA emulsions for use in gloss and semi-gloss interior paints have recently been developed. These have been formulated at pigment volume concentrations ranging from 10 to 25 percent and at a solids content of about 50 percent.

2.3.5.6.3. *Acrylic* latexes are based on a film-forming acrylic copolymer that is tough, adherent, flexible, color-retentive, and resistant to ultraviolet light, alkalies, oil, grease, and moisture. The latex emulsion may be formulated into emulsion paints with a minimum of additives, thus preserving all the desirable properties of the acrylic resin base. Although the acrylics are highest in cost among the three types of latex available, their excellent combination of properties continues to win them an increasing share of the latex paint market. In addition to their excellent durability, they are easily applied, are practically odor-free, dry rapidly, and develop excellent resistance to water within an hour or two after application.

Acrylic latex paints [7] have shown excellent exterior durability in a wide variety of climates, particularly when applied over masonry surfaces. Recently, they have been offered also as exterior house paints on wood surfaces that have first been sealed with a zinc-free oil-type primer. Weathered oil paints on exterior wood surfaces also can be successfully recoated with acrylic latex paint. Excellent primer-sealers for porous surfaces can be formulated from acrylic latexes, over which virtually any type of topcoat may be used, including water paints, oil paints, enamels, varnishes, and lacquers. A new, thermosetting acrylic emulsion polymer is now available which, it is claimed, yields industrial baking finishes of excellent hardness, impact resistance, adhesion, and durability superior to that of premium melamine-alkyds, while equaling the latter in gloss and stain resistance.

2.3.5.6.4. *Latex blends and copolymers* seeking to combine the most desirable properties of each component into a single superior material are receiving a great deal of attention from latex paint manufacturers. Among the more promising recent developments reported are vinyl-acrylic copolymer dispersions that produce films having very good clarity, gloss, flexibility, and water resistance. The vinyl-acrylic latexes are said to possess high pigment-binding ability, excellent thermal and mechani-

cal stability, insensitiveness to electrolytes, and good film-forming ability at relatively low temperatures. They have been formulated into flat wallpaints, semi-gloss enamels, baking coatings, and primer-surfacers. The latter is a sandable first coat which serves both a priming and a surface-smoothing function.

Latex copolymers may be further modified by blending with various compatible resins to obtain other desirable properties, such as improved adhesion, greater toughness, or lower cost. The formulating possibilities, as with conventional resinous coatings, are virtually limitless, and the full potential of versatility and usefulness of modified latex copolymers has only begun to be realized.

2.3.6. Water-Solution Coatings

A natural outgrowth of the wide acceptance of latex paints in the consumer field has been the increased attention being given by the paint industry to the development of water-thinnable coatings for industrial applications, where the protection and durability requirements are more severe. In such cases, a coating material combining the convenience and safety of latex paints with the film integrity of solution-type coatings would be highly useful.

The use of water paints goes back to early civilizations. The ancient Hebrews and Egyptians mixed milk curds and freshly burned lime "on the job" to make a binder (calcium caseinate) for the earth colors with which they decorated the interiors of their houses. This type of painting still persists in some of the rural villages of middle Europe and elsewhere. Colonial Americans often mixed the clabber from skim milk into the whitewash, made of slaked lime and water, which was their main coating material; oil paints, though known and used during this period, were an expensive luxury. Whitewash (see sec. 2.3.9.2) remained in favor as both an interior and exterior coating until the latter part of the nineteenth century, when powder paints for mixing with water before use were introduced. These were the kalsomines, consisting of glue-bound clay and whiting. Although factory-made casein paints in powder form were introduced at about the same time, it was not until the 1920's that casein paints reached large volume usage. Later, to improve the water resistance and durability of casein paints, they were modified with alkyd emulsions. Soon casein assumed a secondary role as emulsifying agent for the alkyd resin in emulsion paints (see sec. 2.3.5.2). The latter gave way to the latex emulsion paints which, ever since their introduction in 1949, have dominated the water-based paint market.

Meanwhile, the quest for a durable water-solution type coating has continued. The basic problem has been to render water-insensitive the film formed from an initially water-soluble resin. In recent years, a number of synthetic, water-soluble resins have been developed which have a built-in chemical reactivity that permits them to be insolubilized (see sec. 3.16.2). These resins will dissolve in water to form a single-phase solution that is infinitely dilutable with water (unlike latex emulsions which are two-phase dispersions of resin-in-water that are capable of only limited dilution). Conversion (insolubilization) of the film laid down from such a solution is accomplished by a chemical cross-linking reaction between polar groups in the water-soluble molecule and an added reactive resin or drying oil, under the influence of heat, oxidizing agents, and/or driers. Although some air-drying types of water-solution coatings have been made, baking is generally required to develop optimum film properties. Baking schedules of about 30 minutes at 300 °F (149 °C) are typical.

All the advantages (and disadvantages) of a water vehicle inherent in latex paints (see sec. 2.3.5.1) apply also to the water-solution type. The fire hazard, toxicity, odor, and expense of organic solvents are eliminated while the advantages of a true solution-type coating, such as good film clarity, high gloss, and excellent film continuity are retained. The latter property is reflected in desirable performance characteristics such as low moisture and gas permeability, and excellent water and salt spray resistance—properties of particular importance in coatings for metals.

The formulation of water-solution type paints does not require the use of wetting agents, thickeners, stabilizers, and bactericides such as are needed in latex paints. The only ingredients generally necessary are pigment, resin, water, and (in some instances) driers. A small amount of high flash aromatic solvent or odorless mineral spirits may be added in some cases to function as a defoamer.

Application of water-solution coatings is usually accomplished by dipping, flow coating, or conventional cold spray; however, hot spray, airless (high pressure) spray, and electrostatic spray also have been employed to some extent.

While the number of satisfactory types of water-solution coatings presently available is not large, technological progress in this area continues. Durable types have been developed which are reported to combine the outstanding gloss and color-retention characteristics of a nondrying alkyd with the hardness, toughness, and adhesion of a drying-oil alkyd; others are reported to possess the hardness, gloss, and durability of the best melamine-alkyds [123] (cf. sec. 3.16.2).

A water-soluble linseed oil that can be formulated into house paints having properties comparable to those obtained with conventional

linseed oil also is available [121].

It is probable that the next few years will see the development of a greater variety of water-soluble convertible resins, including satisfactory air-drying types for use on wood and other surfaces that do not permit baking.

2.3.7. Multicolor Finishes

Multicolor finishes—sometimes called "polka-dot paints"—consist essentially of discrete particles of viscous coating material suspended in water containing a suitable stabilizing agent. The stabilizer is used in an amount sufficient to prevent coalesence of the particles but insufficient to cause their emulsification. A variety of colors and particle sizes and shapes can be incorporated in a single multicolor finish by first preparing separate dispersions of each color and then mixing them in the desired proportions. Each color retains its particular identity in the final mixture for the same reasons that it remains in discrete particle form in its own individual dispersion. The stabilizing agent, when properly chosen and used in the correct concentration, forms a protective film around each coating particle which effectively isolates it from neighboring particles in the aqueous medium, irrespective of their color, provided that certain basic requirements are fulfilled during manufacturing. The literature [8, 9] indicates the following to be the most important factors:

(1) The solvents used in the coating material phase must have a low solubility in water, and the water must have a low solubility in the solvents.

(2) Pigments employed should be non-bleeding either in the solvents used or in water.

(3) The specific gravity of the coating material and of the stabilized aqueous medium must be closely controlled; too great a difference will result in coalescence during storage.

(4) Particle size is largely controlled by the speed of stirring, the size decreasing with increased speed of agitation. The addition of wetting agents or an increase in the amount of stabilizer also reduces the particle size. The viscosity and the temperature of the coating material phase also have an effect, the size of the particles increasing as the viscosity or temperature is increased.

(5) Particle shape depends primarily on the viscosity of the pigmented coating phase but is also affected by the type and amount of stabilizer employed. Higher viscosities, in addition to increasing the particle size, yield globules and filaments instead of spheres.

Although the particle size depends strongly on the speed of agitation, the time of agitation appears to have relatively little effect provided sufficient time for adequate dispersion is allowed. Only gentle stirring is needed after storage; rapid stirring or violent shaking will alter the physical characteristics of the multicolor material and should be avoided.

Most present-day commercial multicolor finishes are based on cellulose nitrate as the chief film-forming component; however, finishes based on alkyd, acrylic, vinyl, and other resins as well as on varnish or oil-base vehicles are possible or available. A Federal specification [10] describes a multicolor lacquer based on a blend of cellulose nitrate with an alkyd resin. A typical commercial interior type blends cellulose nitrate with a rosin ester. Water-soluble organic polymers (protective colloids) such as methyl cellulose or polyvinyl alcohol are the preferred type of stabilizing agent and are effective at relatively low concentrations (0.3 to 5.0%). Various other materials—organic and inorganic, soluble and insoluble—in finely divided form may be employed; the insoluble types must be used in much greater concentration (perhaps as high as 25 percent of the aqueous phase) to be effective.

Multicolor finishes are usually applied as heavily sprayed coats that completely mask the surface. If desired, they may be lightly sprayed to produce a "spatter" coat over a colored base coat. They have also been used as a sprayed coat on paper or textiles subsequently drawn under a doctor blade to produce a striped effect.

The large size and viscous character of the dispersed coating particles in multicolor finishes permits their application to highly porous surfaces without excessive penetration. Thus, dissimilar adjoining surfaces such as masonry and wood, and rough or imperfect surfaces, can be masked completely to give a uniform appearance. Heavy films, 5 mils or greater in thickness, can be sprayed in one application without sagging or wrinkling. Multicolor finishes can be applied to damp (but not fresh alkaline) surfaces without difficulty because their porous nature permits substrate moisture to evaporate without blistering the film. No primer is required for porous surfaces such as wood, masonry, plaster, wallboard, cloth or paper. A primer may be useful, however, over non-absorbent surfaces such as metal.

The limitless color combinations and wide variety of patterns provided by multicolor finishes, coupled with the good durability exhibited by many of the types now available, have led to their use in continually increasing quantities in both interior and exterior applications for hotels, public buildings, industrial plants, homes and furniture.

2.3.8. Fire-Retardant Coatings

2.3.8.1. The primary function and effectiveness of present fire-retardant coatings is in reducing the surface flammability of substrates over which they are applied. To accomplish

this, a fire-retardant coating must itself be essentially nonflammable (non-flame-propagating). Additionally, it may provide a limited degree of shielding and insulation against the heat generated by a fire, thereby delaying the time for the substrate to reach the ignition temperature or—in the the case of a non-combustible substrate—the time for the heat to pass through the substrate to combustibles on the other side.

Not even the best fire-retardant coating can be expected, however, to provide protection for long under the onslaught of a full-scale fire, particularly in a confined area.[1] After the few minutes of initial delay, the chief value of a fire-retardant coating is in reducing the rate of further flame spread rather than in preventing substrate ignition or structural failure in the immediate area under attack by fire. However, while fire-retardant coatings have not proven capable of adding significantly to the fire endurance of buildings and other structures as measured in terms of hours of fire exposure before collapse, the few minutes delay they afford in the early stages of a fire can be of critical importance to the escape of personnel and to the ability of the fire department to control the blaze and minimize damage. It has been aptly said, from the viewpoint of the firefighters who must battle a blaze, that "the first five minutes are worth the next five hours."

The fire-retardant coatings discussed herein should not be confused with heat-resistant coatings (see sec. 3.9.1) of the type employed on surfaces that become or remain hot in normal service (e.g., stoves, boilers, hot pipe liners, etc.). The effectiveness of the heat-resistant coatings depends on their ability to withstand more or less continuous exposure to elevated service temperatures without igniting and without undue impairment of their protective and decorative qualities, rather than on their ability to withstand direct attack by fire; hence they are not properly classed as fire-retardant.

The term "fireproof" is not meaningful when applied to coatings, since it implies a complete and permanent resistance to fire that is not possessed by any organic coating material, no matter how formulated or modified. Reliance upon so-called "fireproof" coatings to the exclusion of other recognized fire-preventive measures and fire-fighting devices can have disastrous consequences.

As for fire-retardant coatings—these are a supplement, not a substitute, for adequate structural design, good housekeeping, care in handling materials, fire extinguishers, sprinkler systems, fire exits, and the fire department.

From the standpoint of formulation and use,

and for purposes of discussion, it is desirable to distinguish between fire-retardant coatings that are merely flame-retardant (subsection 2.3.8.2) and those which provide the additional function of heat insulation (section 2.3.8.3), while bearing in mind that the distinction between the two vanishes, for practical purposes, after the first 5 to 15 minutes of exposure to a large-scale fire. A discussion of these two types follows.

2.3.8.2. FLAME-RETARDANT COATINGS may be described as those which, though decomposed by exposure to fire, serve to retard the spread of flame, although they may not significantly insulate the substrate from the heat generated. They have application in situations where a fire of only short duration is to be expected (e.g., in an area where only small amounts of combustible material are stored), or to keep a localized ignition (such as that from momentary contact with a torch or heated object) from spreading across the exposed surface. Flame retardancy in such coatings is achieved by the use (to the extent feasible) of non-flame-propagating resins and plasticizers, by the use of fusible inorganic salts and pigments (e.g., borax) that form an air-excluding glaze on heating, and/or by incorporating special agents (e.g., brominated compounds) that inhibit the tendency to ignite.

The ignition temperature of a flammable solid is the temperature at which flammable gases are generated and ignited. By incorporating into the material to be protected chemical agents that will convert flammable gases to non-flammable ones as they are generated, an effective degree of flame retardancy can be achieved. Lewis acids, such as hydrogen halides or phosphorus oxides, are effective agents that appear to function in this manner. Although these cannot be used directly in a paint because of their hazardous, corrosive properties, compounds have been developed that are capable of giving off the desired active agent upon heating. Among the most successful of these have been brominated compounds. The bromine can be incorporated directly into the molecule of resins such as alkyds and epoxies. A brominated phenol is compatible with, and may be physically blended with, phenolic resins to render them flame-retardant. Vinyl coatings can be rendered self-extinguishing by using a small percentage of a brominated organophosphate compound, such as tris (dibromopropyl) phosphate, as part of the plasticizer in the formulation.

2.3.8.3. INSULATIVE FIRE-RETARDANT COATINGS also possessing flame-retardant properties have proven to be the most effective type in impeding the progress of a fire. Of these, intumescent coatings that bubble and swell on heating to

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[1] A fire-retardant material incorporating chopped glass fibers is available which does significantly increase the fire endurance of wood or steel structures; however, this material is applied at a thickness (about one-quarter inch) far in excess of that normally designated as a coating.

form an insulating mat between the fire and the substrate have been the most successful. The blowing agents employed in such coatings are sometimes water-soluble compounds that are susceptible to leaching; the coatings therefore may be somewhat water-sensitive and may not retain their full intumescent properties after periods of prolonged (particularly exterior) service.

The degree of protection afforded by a particular fire-retardant coating depends not only on its intrinsic fire-retardant properties (i.e., nonflammability, intumescence, insulative character, strength of charred matrix, etc.) but also on the thickness at which it is applied and on the nature of the substrate. On completely non-combustible substrates, such as ceramics and most metals, application of any organic coating, even a nonflammable one, will increase to some extent the rate of fire spread along the surface—the rate of spread increasing with coating thickness, at least within the practical range. However, since metal surfaces generally require such a protective coating to resist corrosion, the somewhat reduced resistance of the surface to fire must be accepted. In such instances, the reduced surface resistance to fire with increasing thickness may be offset to some extent by the greater heat-insulating effectiveness of the thicker coating. As already pointed out, the heat barrier furnished by the insulative type of fire-retardant coating, though only temporary, can be of vital importance in the first few minutes of a fire.

On combustible substrates, application of a fire-retardant coating of either the flame-retardant or insulating type affords increasingly greater fire protection as the coating thickness is increased [19]. In fact, any coating that is less flammable than the substrate will afford some degree of protection to that substrate. This latter fact sometimes results in erroneously attributing significant fire-retardant properties to a coating material that in reality is contributing only the normal effect of added thickness. Such misevaluation may not only involve the needless expense of paying for a fire-retardancy that is not achieved, but can also create a dangerous sense of false security about the protection afforded.

2.3.8.4. EVALUATION OF FIRE-RETARDANT COATINGS.—Although the ultimate and only fully reliable test for the effectiveness of a particular fire-retardant coating is its actual service performance, several laboratory and large-scale test methods have been developed which give a good indication of the performance that may reasonably be expected from a given material under specified conditions. Such methods are particularly useful in screening out inferior materials that do not merit the expense of large-scale tests or the risk of actual service

tests. Among test methods recognized as useful by those concerned with problems of fire protection are the following:

(1) The standard "tunnel" test developed by Underwriters Laboratories [11, 12].

(2) The radiant panel test devised by the National Bureau of Standards [13, 14].

(3) The flame spread test described in Federal Specification SS-A-118b [15].

(4) The "cabinet method", in which measurements are made of the weight loss and char volume produced by a standard flame that consumes 5 ml of absolute alcohol [16].

(5) The "stick and wick method", in which the weight loss, rate of vertical flame spread, and char height are measured [17].

(6) Various test methods developed by commercial firms, such as the tests with standard bowling pins and with load-bearing steel members used by the Fire Research Laboratory of Union Carbide Chemicals Company [18].

(7) Full-scale experimental fire tests on expendable buildings or structures.

Among the test methods (other than full-scale tests) cited above, the tunnel test is the most generally accepted means available for evaluating the flame-spread characteristics of building materials. The more recently developed radiant panel test was designed to be less elaborate and expensive and has given highly reproducible results, while appearing to correlate fairly well with tunnel results. However, the radiant panel test, largely because of its small scale, has not yet been widely accepted by code officials. Full scale fire tests, while highly informative, are too expensive for routine evaluations.

In interpreting fire tests, it should be borne in mind that different test methods may give different results with different types of materials. For example, a highly reflective coating (e.g., an aluminum-pigmented material) may perform better than a matte coating in the radiant panel test and yet appear inferior by a flame-impingement test. Similarly, tunnel test results may not coincide with results obtained in a load-bearing test or with a test house. Nevertheless, such tests are a necessary prerequisite in the screening of fire-retardant materials. Appropriately applied and wisely interpreted, the results obtained are very useful.

2.3.8.5. SELECTION OF FIRE-RETARDANT COATING SYSTEMS.—From the information that has been presented on the nature and effectiveness of fire-retardant coatings, a basis for their selection may be given.

Flame-retardant coatings (and impregnants, with which this volume does not deal) are useful in the following situations:

(1) To prevent the ignition of combustible fabric surfaces (e.g., draperies or upholstered

furniture) that may inadvertently come into brief contact with a flame or heated object.

(2) To avoid the rapid spread of flame along combustible surfaces such as cellulosic wall-board or ceiling materials.

(3) In combustible enclosures where only small quantities of flammable materials are present, since in such cases the fire (fuel) is likely to burn itself out before the blaze becomes widespread.

(4) To reduce the danger of deadly flash fires in susceptible public areas such as schools, theatres, night clubs, tents, and exhibit buildings, where the loss of life can be very great—although such coatings should by no means be considered to have entirely eliminated the hazard of fire.

Insulative (intumescent) fire-retardant coatings are useful: (1) Where a brief delay in transmission of heat from a fire to a combustible substrate may prevent ignition or serious damage. For example, utility and telephone poles protected with a weather-resistant coating (applied to glass screening stapled to the pole) have withstood repeated brush and grass fires without suffering significant structural damage; such fires usually will burn completely past a stationary object in two or three minutes, an interval during which the coating is capable of providing full protection to the structure.

(2) In aircraft, particularly on large compartmentalized types. Although the effectiveness of fire-retardant coatings for aircraft has not been fully evaluated, there is reason to believe that in some kinds of fires aboard aircraft in flight, personnel might have time to bail out or possibly make a safe forced landing if vital areas of the aircraft could be insulated from the heat of the fire for only a few minutes. Despite the existence of a definite interest in such coatings, their use on aircraft has not been widespread.

(3) On ground structures within quick range of fire-fighting equipment, as at airfields and military installations, which may be saved from severe structural damage if ignition of combustible substrates can be delayed long enough for the fire-fighting equipment to be brought into action.

(4) To provide heat insulation as well as flame retardance on walls and ceilings of schools, office buildings, and other heavily populated compartmented buildings, where every minute of delay in the transmission of heat from one room to another can be of vital importance in permitting personnel to escape, even though the ultimate fate of the structure itself may be little affected.

A number of Federal and Military Specifications relating to fire- and flame-retardant coatings are available. Although all of these specifications refer to "fire-retardant" coatings, many of the coatings may be more aptly described as flame-retardant according to the criteria set forth in the preceding paragraphs, since their primary function is to reduce flame spread rather than to insulate the substrate from the fire. For example, flame-retardant coatings of conventional coating thickness rather than heavy intumescent fire-retardant coatings are specified for use on metal bulkheads and overheads of navy ships [19, 20, 21, 22, 23, 24], where the primary concern is to minimize flame spread via the paint (both directly and through heated bulkheads) and to limit the production of toxic decomposition products in the confined space aboard ship. On the other hand, fire-retardant coatings of the intumescent type [25, 26] have generally been the most effective and are usually specified for wood surfaces, where the combustible nature of the substrate requires the greater protection that is afforded by the insulative type of fire-retardant coating in order to avoid quick ignition.

2.3.8.6. IN SUMMARY, it should be pointed out that while there exists general agreement as to the ability of fire-retardant coatings to impede the progress of a fire, there is considerable question as to the extent and effectiveness of the protection provided. It must be emphasized that the protection afforded by even the best fire-retardant coating is limited to the early stages of a fire. However, to the extent that the delay afforded enables personnel to escape and fire-fighting equipment to be brought into action, valuable protection is achieved. Once the fire reaches full-scale proportions, no coating will appreciably affect the course of the blaze.

In many applications, flame-retardant and insulating types may perform equally well. In fact, it may often not be known whether a given fire-retardant paint is one type or the other unless specific information is provided by the manufacturer. There are situations, also, in which a coating of demonstrable fire-retardant effectiveness may be unsatisfactory for certain applications because of deficiencies in conventional paint properties such as appearance, durability and weathering resistance; or the thickness required may be too great for some applications (as aboard high-speed aircraft, where weight must be kept to a minimum). It is probable that the shortcomings of fire-retardant coatings with respect to some desirable paint properties have been a strong factor in slowing their widespread adoption.

Although there remains much room for improvement in the formulation and efficacy of fire-retardant paints, continuing developmental work is being carried on by a number of paint manufacturers, and it is likely that the role of

such paints will become increasingly important as their effectiveness is increased.

2.3.9. Cold Water Paints (Inorganic)

Water-base paints utilizing organic binders of the latex type and water-soluble type were discussed in sections 2.3.5 and 2.3.6, respectively. The present section briefly describes two other types of cold-water paints which, though inorganic or largely inorganic in nature, have important application in the coatings field.

2.3.9.1. CEMENT-WATER PAINTS are very useful for concrete and masonry surfaces (see secs. 2.4.3 and 4.4). They are composed chiefly of white portland cement together with some hydrated lime or siliceous aggregate or both, depending on the requirements of the application. Cement-water paints of two types (medium or high cement content) and two classes (without or with siliceous aggregate) are described by Federal Specification TT–P–21 [32]. The lime contributes easier brushability and, if not used in excess (not more than 30 percent by weight), assists in obtaining a hard, weather-resistant coating. The aggregate (usually a white or light-colored silica sand) is very useful in cement-water paints that are to be applied to open-textured masonry surfaces where filling is needed; two parts by volume of portland cement to one part of aggregate produces a good fill coat composition. For use as a "grout coat" on very coarse surfaces such as cinder block, equal parts by volume of cement and sand are most effective. Proprietary formulas for general-purpose cement-water paints often add small proportions of other ingredients to the white portland cement and lime. For example, calcium chloride may be added for its hygroscopic effect in drawing moisture from the air, which promotes proper curing and hardening. Titanium dioxide or zinc sulfide pigments may be added to improve the wet opacity, and colored pigments may be added to produce tinted paints. About one percent of calcium stearate may be incorporated to provide some degree of water repellency in the dried paint.

The mixture of solid ingredients is furnished as a dry powder that needs only to be mixed with water to prepare it for use. The dry material should first be made into a stiff paste by adding small portions of water with continuous stirring, after which additional water should be gradually stirred into the mix until a consistency resembling that of rich cream is obtained (except that a slightly thinner consistency is desirable for the first coat applied on open-textured masonry surfaces). Cement-water paints normally remain in usable condition for three or four hours after being prepared for use; however, small additional amounts of water need to be added (with thorough stirring) during this period to counteract the tendency of the paint to stiffen as a result of its reaction with the water and the loss of water by evaporation.

Concrete and masonry surfaces that are to receive cement-water paints should be cleaned free of dirt, oil, grease, and efflorescence as described in section 6.4. Since cement-water paints are completely resistant to the moisture and alkalinity in concrete, little or no aging of the surface is required. Previously painted concrete or masonry surfaces must be cleaned free of all masonry coatings, whitewash, or weak, crumbly cement paint (see sec. 6.6.4.3).

Application of cement-water paints is best accomplished with a stiff fiber brush which permits the paint to be scrubbed into the voids of the surface. The surface should be uniformly damp but not wet with water before the paint is applied. The paint should be applied in two coats with at least 24 hours allowed between coats. The first coat should be dampened with water before applying the second coat. Excessively thick or thin coats are undesirable. Thick coats are somewhat prone to crack or chip from the substrate; also, it is more difficult to apply them uniformly. Thin coats lack opacity and durability. Too wet a mix will produce a powdery texture when dry, as well as too thin a coating. The proper spreading rate for cement-water paints depends on the texture of the surface; as a rough guide, the spreading rate may be about 100 square feet per gallon for two coats on smooth masonry and about 50 square feet per gallon for two coats on rough masonry.

Proper curing and hardening of cement-water paint into a durable, stress-free coating that will not be prone to cracking, crumbling, or powdering depends on the continual availability of adequate moisture for reaction with the portland cement, especially during the first few days after application. To accomplish the necessary damp curing, the painted surface should be wet down with a fog spray two or three times a day, starting within 6 to 12 hours after application of the first coat and continuing for at least 48 hours after application of the final coat.

Properly applied and damp-cured, cement-water paints provide a durable coating for exposed concrete or masonry surfaces above or below grade, inside or outdoors.

2.3.9.2. WHITEWASH, for centuries before the advent of modern coating systems, was widely used as a readily available, inexpensive, general-purpose coating for interior use on wood, plaster, concrete, masonry, glass, and metal. While lacking the durability and the protective and decorative qualities of many present-day coatings, whitewash still finds some use as a low-cost, easily applied coating for

sheds, fences, tree trunks, concrete curbs, gasoline station islands, brickwork, cinder block, and other noncritical applications in mild environments where its flat, extreme chalky-white appearance gives a clean, pleasing effect. In particular, whitewash still finds favor as a coating for the interior walls and ceilings of dairy barns, for farm implements and structures, and as a light- and heat-reflective coating for coal tar pitch or asphaltic surfaces to reduce their tendency to soften, sag, wrinkle, or run when exposed to direct sunlight in hot climates.

Whitewash in its simplest form is prepared by slaking quicklime or soaking hydrated lime in water, the latter method being preferable because of its greater safety, convenience, and uniformity of product. Approximately 8 gallons of stiff lime paste are produced by slaking 38 pounds of quicklime with 8 gallons of water, or by soaking 50 pounds of hydrated lime in 6 gallons of water. Before use, sufficient water is stirred into the paste to obtain a thin consistency resembling that of whole milk. To improve durability, other materials are nearly always added to the mix. For general use on wood, glass, and metal, the additives most often used are common salt and calcium chloride, which are dissolved in the water to be used for diluting the original lime paste. The use of calcium chloride rather than salt reduces the tendency of the whitewash coating to chalk. For use on concrete and masonry, more satisfactory results are obtained with a whitewash consisting of equal parts by weight of hydrated lime and white portland cement (a composition approaching that of the cement-water paints described in the preceding section) with sufficient water to produce a mixture having the consistency of heavy cream. Other materials which may be added to whitewash for various purposes include casein plus formaldehyde for interior walls of dairy barns, casein plus borax to produce a fire-retardant coating, animal glues for use on plaster, titanium or zinc sulfide pigments to improve opacity, and iron oxide pigments for tinted coatings. More detailed information on whitewash is available in a bulletin by the National Lime Association [126].

2.4. Primers

A primer is applied as the first coat of paint on the substrate (sometimes preconditioned) to be painted. Its chief function is to provide a satisfactory bond between the finish coats and the substrate. The primer may also be called upon to impart other important properties to the system, such as corrosion resistance, water resistance, substrate sealing, enamel hold-out, and some degree of substrate filling and hiding. The choice of vehicle and the proper pigment-binder ratio are important considerations in obtaining the required degree of wetting, penetration, and adhesion. The formulation is usually such as to yield a satin surface to which topcoats will adhere well; pigment volume concentration is intermediate between that for gloss and dead flat finishes. The pigments employed are similar to those used in finish coats, except for the addition of corrosion-inhibiting pigments in metal primers.

2.4.1. Wood Primers

Primers for wood that is to withstand exterior exposure are usually of the oil or oleoresinous type. The primer (or undercoater, as it is often called in wood painting) serves to seal the wood pores, so that good hold-out and adhesion of topcoats is obtained. The vehicle is usually a blend of heat-bodied and raw or refined oils (see sec. 2.2.1), usually linseed, modified with a small amount of resin. Brushing characteristics, control of penetration into the wood, and leveling of the paint film are largely dependent on the ratio of raw to bodied oil. With larger proportions of raw oil brushing properties are improved and degree of penetration is increased, but leveling is poorer. Conversely, larger proportions of bodied oil improve leveling properties, but reduce ease of brushing and penetration. A 1:1 blend of raw oil with bodied oil of consistency approximately "Z" on the Gardner Scale (equivalent to about 23 poises) has been widely used.

Zinc oxide is sometimes used in the pigment portion in place of part or all of the resin in the vehicle, although its use in wood primers is controversial. Chalk-resistant titanium pigment, white lead, and extenders usually comprise the pigment portion. An excellent primer for exterior wood is covered by Fed. Spec. TT–P–25 [111].

Exterior oil paints may be made into so-called "self-primers" by thinning with turpentine or mineral spirits and/or by adding raw linseed oil.

Water-based coatings have not, as yet, proven satisfactory as wood primers. However, some water-based paints (e.g., an acrylic or a polyvinyl acetate latex paint) can be successfully applied on wood that has been primed with an oil paint.

2.4.2. Primers for Metal

Primers are nearly always required for adequate adhesion of topcoats in coating systems for metals. They may be either air-drying or baking types. Most metals need extra protection against corrosion which necessitates the

incorporation of corrosion-inhibiting pigments into the primer. The manner in which such pigments function is discussed in section 2.3.1.5. The choice of pigment depends on the metal to be protected. A metal conditioning pre-treatment (see sec. 6.3.2), such as phosphatizing, when used prior to application of the primer, greatly improves primer adhesion and corrosion resistance; under these conditions, corrosion resulting from scratches or other breaks in the coating is confined largely to the immediate area of the scratch or break.

2.4.2.1. PRIMERS FOR IRON AND STEEL are based on a variety of rust-inhibitive pigments in a suitable vehicle, such as linseed oil, an alkyd resin, or a phenolic resin-drying oil varnish [27, 28] (also see list in sec. 8.1.4 and summary charts in sec. 8.2). Raw linseed oil possesses the best penetrating properties and is essential where complete removal of surface corrosion products has not been feasible. Among pigments often used in primers for iron and steel are red lead, basic lead chromate, blue lead, and zinc yellow, together with iron oxide pigments and silicate extenders. The time-honored superiority of red lead is believed to result from its ability to combine chemically with the iron or steel substrate to form a hard, highly adherent, moisture-impervious coating that passivates the substrate against corrosion. The use of a basic lead silico-chromate pigment to impart corrosion-inhibiting properties not only to primers but also to intermediate and finish coats is discussed in section 2.3.1.5.

The choice of pigment and vehicle depends on the nature of the application. For outdoor steel structures, primers based largely on red lead [27] in a linseed oil or long oil-alkyd vehicle are widely used (also see 4.3.1.1). In marine areas, a long oil-phenolic vehicle is often preferred. Under severely corrosive conditions, vinyl primers [143, 144, 145] in an all-vinyl coating system give durable service (see sec. 4.3.1.2). Automotive primers often contain iron oxide as the chief pigment in a short or medium oil-alkyd baking vehicle; amino resin-alkyd vehicles are also used. Zinc-rich paints containing high percentages of zinc dust (see sec. 2.3.1.5) in an epoxy, epoxy-polyamide, polyurethane, or other alkali-resistant vehicle are being successfully used as primers for the undersides of automobiles, for underwater structures, and for other types of severe marine service where their excellent corrosion-resistant properties justify their higher cost. Industrial primers for machinery, refrigerators, washing machines, and other appliances are generally baking types based on short oil-alkyd vehicles or newer vehicles such as epoxy ester-modified alkyds. (A discussion of alkyd resins is given in sec. 3.4).

Water-base metal primers, mostly baking types, have been successfully formulated for some applications. For example, a styrene-butadiene latex containing iron oxide pigments plus china clay and barytes extenders is used as the primer on some automobiles. A water-solution type primer is available for use underneath a recently-developed, water-solution type industrial topcoat (*cf.* sec. 2.3.6.). In these types, the water-soluble resin is converted to a cross-linked, insoluble coating by baking.

2.4.2.2. PRIMERS FOR GALVANIZED IRON AND STEEL are most effective when formulated with high percentages of zinc dust as the chief pigment [29]. The zinc dust, in addition to aiding adhesion, may provide some degree of cathodic and barrier layer protection to the underlying iron or steel (see sec. 2.3.1.5).

2.4.2.3. PRIMERS FOR ALUMINUM are based largely on zinc chromate and zinc tetroxychromate as the corrosion-inhibiting pigments in a variety of vehicles, including phenolic alkyds, styrenated alkyds, and polyvinyl butyral. The latter is combined with phosphoric acid and alcohol just before use to yield a so-called wash primer or metal pretreatment coating [30] which provides both a phosphatizing and a priming action that gives excellent results (see sec. 6.3.2.5). A conventional spray-applied, fast-drying zinc chromate primer [88] or a low moisture sensitivity type [54] may be used [122] over the wash primer to provide an anchor coat for the finish coats. A relatively slow drying alkyd-base zinc chromate primer, for brush or spray application on chemically cleaned bare metal, is covered by Fed. Spec. TT–P–645 [89] (see summary chart in sec. 8.2); this primer is particularly suitable as an undercoat for alkyd enamels and for marine service. Lead-containing pigments are not considered satisfactory in primers for aluminum because of the possibility of a galvanic action between deposited lead and the aluminum which would result in pitting of the surface.

2.4.2.4. PRIMERS FOR MAGNESIUM must be carefully formulated to obtain adequate adhesion and corrosion resistance. Zinc chromate is the preferred corrosion-inhibiting pigment [31]. Pigments such as red lead and other lead pigments (except lead chromate) that perform excellently in primers for steel may promote the corrosion of magnesium. Acidic vehicles may cause gassing at magnesium surfaces and so destroy adhesion and accelerate corrosion. Satisfactory vehicles have been based on phenolic-modified alkyd resins [54, 88], phenolic-tung oil varnishes, epoxy baking resins, chlorinated rubber, vinyl copolymer resins, and polyvinyl butyral resin. The latter is usually a non-acid type, although a polyvinyl butyral wash primer with reduced acid content

is sometimes used on adequately pretreated surfaces. Whenever magnesium is to receive an organic protective coating system, proper surface pretreatment (usually chromating) before application of the primer is of great value (see sec. 6.3.5).

2.4.3. Masonry Primers

Primers for masonry are not a well-defined class of specially formulated materials as are primers for metal. They are usually made simply by addition of an appropriate thinner to the topcoat paint. Latex-base paints [5, 6, 7], which are now the most widely used type for masonry surfaces, are thinned with suitable amounts of water. Paints made with portland cement and lime [32] are also thinned with water. Oleoresinous [33] and synthetic resin types, including the various solvent-thinned rubber-base products [34, 35], require specific organic solvents which are usually identified in specifications for the materials and on the container labels. As a general rule, ordinary mineral spirits can be used to thin oleoresinous paints whereas thinners of greater solvent power, such as aromatic and chlorinated hydrocarbons (along with some aliphatic hydrocarbon diluent), are required for such products as the styrene-butadiene copolymers (non-latex, synthetic rubber type), chlorinated rubber, and others.

Apart from primers made as indicated above, there are a limited number of products made expressly for priming purposes. For example, special primers have been developed to combat mottling of deep-colored masonry finishes. Others are designed to alleviate some of the difficulties encountered in the painting of chalked masonry surfaces. Although removal of the chalk is the only sure answer (see sec. 6.4.6), some benefit can be obtained by the use of special oleoresinous anchor coats (e.g., a phenolic resin-tung oil varnish), by use of an emulsion type surface conditioner containing special wetting agents, or by stirring some oil (e.g., boiled linseed oil) into latex-base paints just before applying them.

Latex primers and paints are relatively non-sensitive to water and alkali and provide excellent sealing of concrete, brick, cinder block, stucco, and other porous masonry surfaces. They may be applied over damp, relatively unaged masonry surfaces without difficulty. (Fresh, uncured surfaces should not, of course, be painted). Although permeable to water vapor, latex primers are not affected by passage of the vapor through them or through the surface on which they are applied. In addition to thinning latex paints with limited amounts of water to make them suitable for masonry priming purposes, it is good practice also to

dampen the porous surface and thereby satisfy its water demand.

Oleoresinous primers and paints for masonry surfaces are generally capable of good performance only when applied to well-aged, clean, dry surfaces that can be expected to remain reasonably dry during service. Otherwise, discoloration, blistering, peeling, and other defects may occur.

Resin-emulsion paints used as masonry primers in the past have been largely replaced by the more alkali-resistant latex types. However a few alkyd resin emulsion paints are available [36], and some developmental work on these materials is continuing.

Cement-water paints [32], despite their low strength and chalking tendency as often formulated and applied, are used on open-textured masonry surfaces because of their low cost and their complete freedom from difficulties arising from dampness or alkalinity in the substrate. Because they are highly permeable to water vapor but are virtually unaffected by water, they are suitable for application to interior masonry below grade (e.g., basement walls of cinder block, etc.). With proper formulation and wet-curing, their durability is quite good. (See sec. 2.3.9.1).

Under conditions of prolonged immersion, as in swimming pools, primers and paints based on a chlorinated rubber vehicle [35] or on a solvent-type styrene-butadiene rubber vehicle have been offered and have achieved a considerable measure of success.

2.4.4. Primers for Plaster and Wallboard

Unlike masonry primers which usually are simply thinned topcoat paints, primers or primer-sealers for plaster and wallboard are usually specially formulated materials that differ from finish coats in pigment-binder ratio and vehicle composition. The term "primer-sealer" emphasizes the important sealing function to be performed on porous surfaces (see sec. 2.3.5.3). Both latex-base and oleoresinous [37] types of primer-sealer are available. Either type may be over-coated with virtually any type of finish coat—latex, oil-base, or alkyd. A thinned latex-base finish coat paint such as that described by Federal Specification TT–P–29 [38] is sometimes used as a primer.

Although the latex-base primer-sealers are relatively new materials, they are widely used because of their fast dry, excellent sealing properties, and superior water and alkali resistance. They may be applied on only briefly aged plaster surfaces; however, a drying period of at least two weeks is highly desirable. They are particularly well-suited for application on gypsum wallboard [127] because of their nonsensitivity to the alkalinity in the plastered tape joints employed and because they do not raise the nap

of the outer paper layer as do oleoresinous types. A phenolic emulsion-type dry wall primer also is available for use on gypsum wallboard.

Oleoresinous primer-sealers, while less resistant to water and alkali than the latex types, give satsfactory results when applied to dry, well-aged plaster surfaces (60 to 90 days of aging are usually required). The oleoresinous primer-sealers offer the good brushability, good flow-out and leveling characteristics, and good

adhesion typically associated with oil-base paints. On inferior plaster having a powdery or chalky surface, oleoresinous primers provide better wetting and adhesion than is obtained with the latex types. As always, as much of the chalk as possible should be removed before painting.

Composition-board and other non-alkaline wallboards (see sec. 6.5.2) may be sealed with either the latex or oleoresinous type of primer-sealer with good results.

2.5. Bituminous Coatings

2.5.1. Hot Applied

Bituminous coatings based on coal-tar pitch or on natural or petroleum-derived asphalt find wide use in underground and underwater applications, in roofing, and for general waterproofing and damp-proofing applications on concrete and metal in buildings, dams, penstocks, reservoirs, tanks, sewage disposal plants, etc. Their usefulness stems chiefly from their virtually complete imperviousness to water and moisture in the thick coats (3/32 to 1/2 inch) that can be economically applied. As hot melts or hot-applied mastics, they are the most widely used coating materials for the protection of buried or submerged steel pipe and other ferrous metal-work.

Coal-tar pitch enamels and asphalt mastics for hot application are made by compounding the bituminous base material with mineral filler. The mineral filler permits application of a thicker coating, raises the softening temperature, and reduces the tendency of the coating to crack and disbond at low temperatures. Coal-tar pitch, while superior to asphalt in water imperviousness and dielectric strength, is more susceptible to temperature changes and to the deteriorative effects of atmospheric weathering. Therefore, pitch is the preferred bitumen for underground and underwater applications, while asphalt is more widely used in above-ground and roofing applications. The low temperature working limit for coal-tar coatings has been extended down to about —20 °F by incorporating plasticizer into the pitch to impart some flexibility.

2.5.2. Cut-Backs

Pitch and asphalt may be "cut back" with suitable coal tar or petroleum hydrocarbon solvents to give coatings that may be readily cold-applied. While the straight "cut-backs" afford little protection because of their susceptibility to cracking from hardening and shrinkage during atmospheric exposure, they are useful as primers on surfaces that are to receive hot melt coatings of the same substance. Also,

when cut-backs are compounded with suitable mineral fillers, such as asbestos, durable products are obtained which are used extensively as protective coatings in roofing and waterproofing applications. An asphalt roof coating of this type is covered by Fed. Spec. SS–A–694 [112].

2.5.3. Bituminous Paints and Varnish

Useful yet relatively inexpensive coatings are obtained by combining pitch or asphalt with resins and/or drying oils in a suitable solvent medium to yield bituminous paints and varnishes. Such coatings provide good protection against industrial and corrosive environments at low cost. Although dark in color and quick to dull upon weathering, they can maintain their protective qualities for long periods provided they have been carefully applied (at least three coats) in a manner that ensures freedom from pinholes and holidays (non-wetted areas). An asphalt varnish of general utility is described by Fed. Spec. TT–V–51 (see summary chart in section 8.2); while this varnish is particularly suited for painting interior water and gas pipes, it may also be used outdoors if sheltered from the sun.

Bituminous paints and varnishes may be applied over old oil paints, but oil paints should not be used over the bituminous types. Oil paints tend to crack and flake off from bituminous undercoats because of their inability to follow the greater thermal expansion and contraction of the bitumen. Furthermore, the dark-colored bituminous material will eventually bleed through an oil or oleoresinous topcoat (see sec. 7.2.2.3).

2.5.4. Emulsions

Bituminous emulsions are available which possess many of the desirable properties of both bituminous and water-base coatings. Certain asphalt and coal tar emulsions are superior in weathering characteristics to their "cut-back" counterparts. In fact, clay type asphalt-base emulsions, such as that included in Mil. Spec.

MIL–R–3472 [113], when used as roof coatings, exhibit the best durability among bituminous coatings. Asphalt-base emulsions for use as thick protective coatings for metal are covered by ASTM D 1187–56 [114]) ; the type A material is a quick-setting type for use where the coating is to be subjected to water immersion, while the type B material is for use on surfaces exposed to the weather only.

A coal tar emulsion that may be used by itself or as a topcoat over coal tar mastics or coal tar enamel to improve their resistance to sunlight is covered by Military Specification MIL–

C–15203 [116]. This coating is intended primarily for atmospheric exposure; it should be allowed to dry for several months in good weather before immersion in water.

2.5.5. References

For a more detailed treatment of the subject of bituminous materials and coatings, the reader is referred to the works of Abraham [39] and to the manuals [40, 41] and specifications [42, 43] of those Departments and Associations in which these materials have an important role.
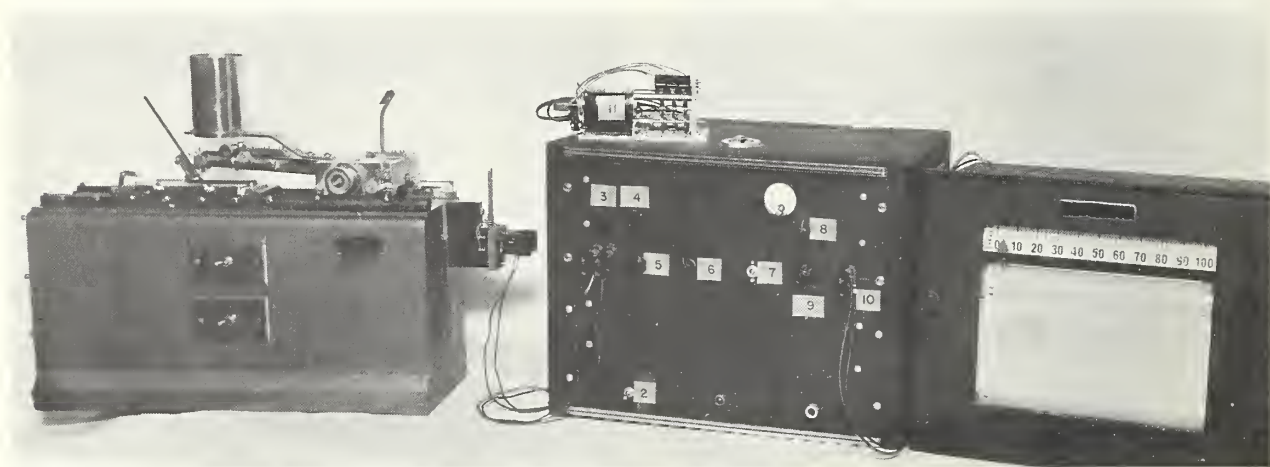
FIGURE 2.1. *The NBS Integrometer (center) increases the speed, ease, and precision of adhesion measurements with the Adherometer (left), by converting the variable stripping force into electric impulses and adding them to give an output that is indicated on the recorder.*
(Roberts, A. G., and R. S. Pizer, Protective coating adhesion measurement using an electronic averaging device for the Adherometer, ASTM Bulletin No. 221, April 1957, pp. 53-58.)
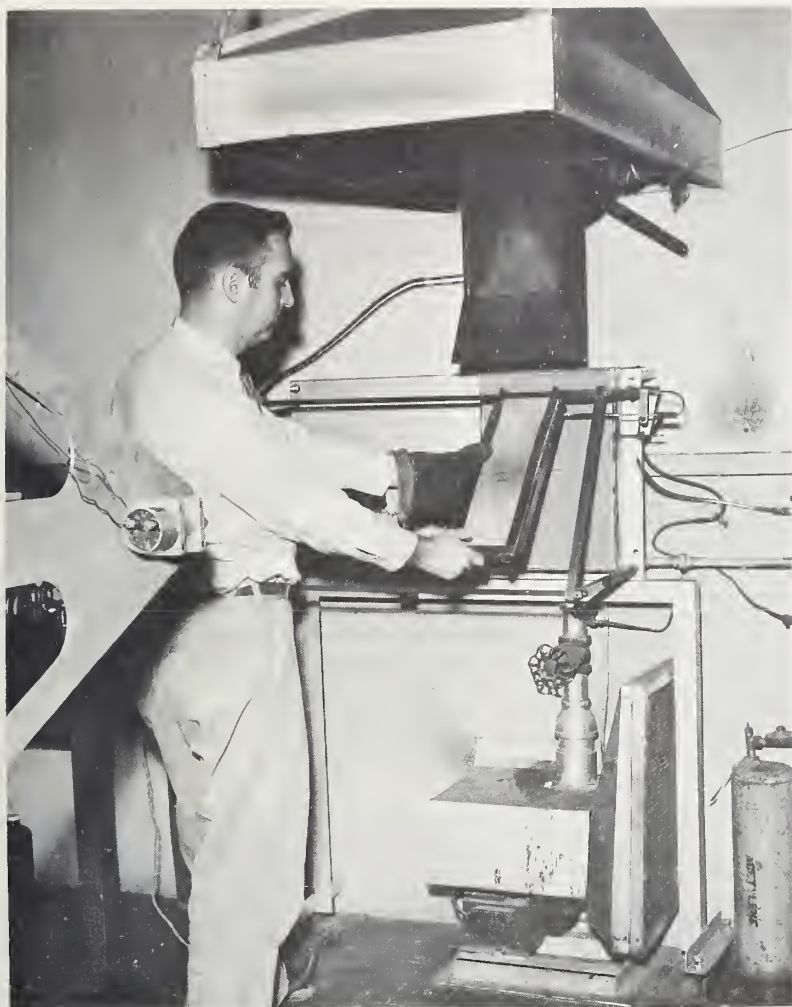
FIGURE 2.2. *NBS radiant panel flame spread apparatus for studying surface flammability of combustible materials as described in ASTM Method E 162-66T; ignition is forced at top of specimen so that combustible gases and flames rise while flame front progresses downward. Rate of flame travel and rate of heat release are measured. (See text, p. 23.)*

FIGURE 2.3. *Explosion of cellulose nitrate film from decomposition in storage.*
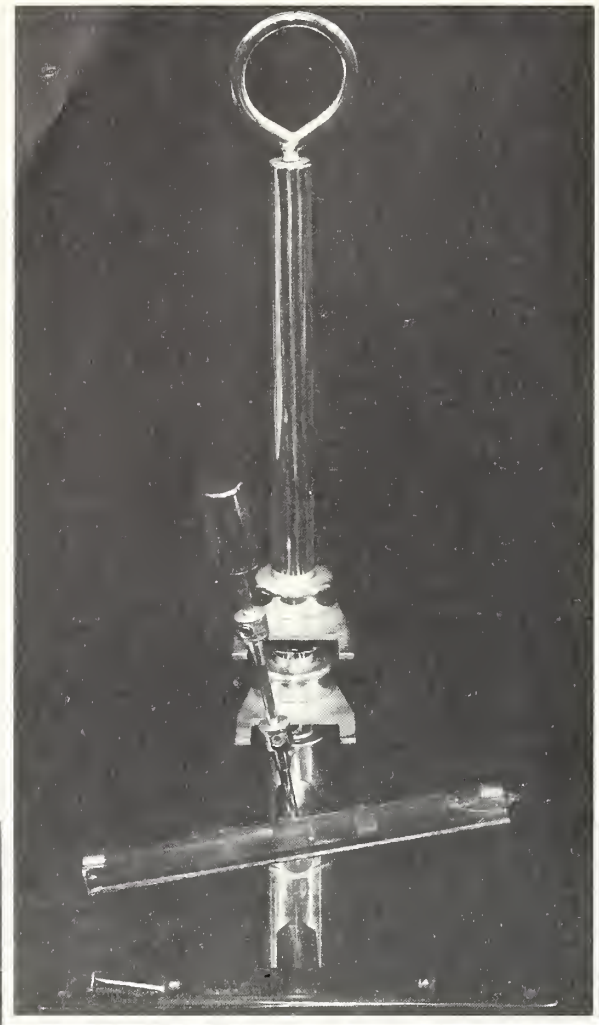
FIGURE 2.4. *Interchemical bubble viscometer for measuring consistency of paints.*

FIGURE 2.5. *Washability machine for measuring scrub resistance of paints as described in ASTM Method D 2486-66T.*

3. Properties of Synthetic Resins for Coatings

3.1. General Nature of Synthetic Resins

Synthetic resins are polymeric substances of high molecular weight made up of repeating molecular structural units, usually in the form of chains, with a terminating group at each chain end. As many as a hundred thousand or more repeating units may be combined into a single polymer molecule having a molecular weight in the millions. The most useful high polymers, however, are those with average molecular weights ranging from a few thousand to several hundred thousand, corresponding to a degree of polymerization (average number of repeating units per chain) ranging from about a hundred to several thousand.

The polymer chains may be linear, branched, or crosslinked—or some combination of these —depending on the functionality and reactivity of the monomers from which they are formed and on the manner of polymerization. Whatever the basic chain structure, the solid polymer consists of a closely entangled mass of kinked, coiled, sometimes folded, and variously oriented and ordered polymer chains. The physical properties of the bulk polymer are largely determined by the structure of the polymer chains, their molecular weight (chain length), and the nature and magnitude of the intermolecular forces (van der Waals forces) which are operative between chains in close proximity. The chemical properties of the polymer depend on the chemical nature, i.e., the reactivity and bond energies, of the linkages between chain segments, and on the reactivity of side groups and end groups.

3.1.1. Polymer Structure and Properties

In *linear polymers* the molecular chains, although closely entangled, are separate entities. Hence, they are relatively free to kink (shorten), uncoil (stretch), or slip past each other (undergo plastic flow or permanent deformation) under the influence of applied stresses; they acquire greatly increased mobility (soften) as the temperature is raised; and they can be molecularly dispersed (dissolved) in suitable solvents. Linear polymers, therefore, are permanently fusible and soluble, and are described as *thermoplastic materials*. (A notable exception to this generalization is polytetrafluoroethylene which, though linear and classified as thermoplastic, is neither fusible nor soluble in the ordinary sense.)

When the polymer chains have a regular molecular configuration that is conducive to alinement and close packing, the bulk polymer exhibits crystalline properties to a degree determined by the number, size, and arrangement of the crystallites (highly ordered regions.) While polymers may be simply characterized as crystalline (ordered) or amorphous (disordered) on the basis of whether or not they are capable of yielding definite X-ray diffraction patterns, seldom if ever is a polymer completely one or the other. Instead, highly ordered regions, amorphous regions, and regions of intermediate order or disorder are randomly interspersed, and the ratio of crystalline to amorphous material strongly influences the mechanical properties of the polymer. This is because the close proximity of the polymer chains in crystalline regions gives rise to large intermolecular forces which are manifest as greater stiffness, greater tensile strength, a higher softening temperature, and increased resistance to swelling and solvation in the crystalline polymer as compared to its amorphous counterpart.

Crystallinity in a polymer mass may be induced or extended by stretching (cold drawing.) Stretching an amorphous polymer causes an alinement of polymer chains which may produce some oriented crystallites. The drawing of a crystalline polymer causes the existing crystallites to become oriented along the axis of draw and may form still more crystallites. Orientation substantially increases the tensile strength of the polymer, greatly enhancing its suitability as a fiber. Typical crystalline polymers are polyethylene, polypropylene, polyvinyl chloride, polyvinylidene chloride, polytetrafluoroethylene, and linear polyamides. Among typical amorphous polymers are polystyrene, acrylic resins, and copolymers in general (the latter are amorphous because the random and irregular spacing of the component monomeric species prevents the close packing of polymer chains).

In *crosslinked polymers*, the molecular chains are tied together and their mobility is reduced by the many primary valence bonds between chains. Such polymers are described as thermoset materials and are infusible and insoluble, except under chemical attack or degradation. It is evident that the degree of stiffness and associated properties exhibited by a crosslinked material will depend on the extent of the crosslinking. Thus, a material with few cross links between chains will deform relatively easily. The cross links serve to limit chain slippage, permitting the material to exhibit rubbery or elastic properties; such a material may swell markedly in certain solvents yet not dissolve in them. Highly crosslinked materials, on the other hand, exhibit a high degree of stiffness, infusibility, and insolubility.

Branched polymers are those in which basically linear molecular chains acquire long-chain side groups as a result of the random activation of sites along the already polymerized main chain or by the introduction of occasional trifunctional groups during the polymerization process. The side chains are similar in molecular structure to the parent chain and may grow to considerable length, with side chains of their own, so that a highly branched structure with properties resembling crosslinked polymers may be built up.

Crosslinked or thermosetting polymers, because of their infusible and insoluble character, are generally superior in overall chemical resistance and dimensional stability to the thermoplastic types. The thermoplastic polymers, however, offer a wide range of properties and a versatility of formulation and application that find wide use in the coatings field. Coatings based on thermosetting resins require heat and/or chemical curing agents to develop their full crosslinking and cure. Coatings based on thermoplastic resins are deposited as continuous, cured films upon evaporation of the solvents in which they are dispersed or dissolved.

Coatings based on drying oils (see section 2.2.1) cure by a combination of oxidation and polymerization to form a loosely crosslinked and fairly flexible structure in which neighboring molecules are tied together through the reactive unsaturated groups occurring toward the middle of the fatty acid radical. This process by which drying oils harden is often described as *auto-oxidative polymerization*.

3.1.2. Functionality and Polymerization Mechanisms

3.1.2.1. FUNCTIONALITY.—The type of structure obtained when a given material or group of reactants is polymerized depends on their chemical reactivity and functionality. Functionality may be defined as the number of active sites (primary valence bonds) per molecule available for reaction under the conditions imposed. In order for polymerization to take place, the functionality of each reacting molecule must be at least 2; that is, there must be two or more functional or reactive groups per molecule. A functionality of 2 results in the formation of linear polymers. Branched polymers also may be formed when the functionality is essentially 2, through the random activation of sites as discussed previously. When the average functionality of the reactants is greater than 2 (not necessarily an integer), crosslinked polymers are formed. The manner in which functionality determines the type of polymer structure obtained will be apparent from the following discussion of the main types of polymerization.

3.1.2.2. ADDITION POLYMERIZATION.—Bifunctionality arising from the opening of a double bond in an unsaturated monomeric material, such as ethylene ($CH_2{=}CH_2 \to -CH_2{-}CH_2{-}$), or styrene ($CH{=}CH_2 \to -CH_2{-}CH_2{-}$), affords an opportunity for chain growth by a simple addition process in which successive monomer radicals become attached end-to-end to form a linear polymer molecule, without the splitting off of a by-product molecule. Occasional random activation of sites along a polymer chain permits the growth of side chains, again by an addition process, so that various degrees of branching may occur in otherwise linear polymers. If the monomer is polyfunctional (functionality greater than 2), then the addition reaction will proceed *between* growing chains as well as by end-to-end addition, so that a three-dimensional, crosslinked structure will be built up. For example, the tetrafunctional p-divinyl benzene $CH{=}CH_2$ quickly forms a highly crosslinked, rigid, insoluble polymer which has little practical use. If, however, a very small quantity of p-divinyl benzene (as little as 0.002 percent) is incorporated into styrene monomer, then a lightly crosslinked polymer is formed in which the linear polystyrene molecules are tied together through an occasional divinyl benzene cross link. Even with so few cross links, complete dispersion of the polymer is no longer possible, so that solvents that would dissolve the linear polystyrene will only swell the crosslinked type. The limited degree of crosslinking also raises the heat distortion point of the polymer and reduces the tendency toward cold flow, without seriously affecting the basic desirable properties of the material.
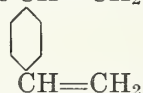
In addition polymerization the growth of individual chains is propagated by a free radical mechanism and is very rapid—an activated monomer molecule may grow to a terminated polymer chain in a small fraction of a second. However, complete conversion of monomer to polymer may require several hours. During this time, monomer and polymer coexist while the monomer material is gradually used up in the production of polymer chains. The molecular weight obtained depends on the conditions of the reaction and on the presence of inhibitors, monofunctional reactants, and other chain terminating mechanisms. Careful control of monomer purity, catalyst, and reaction conditions is required in order to obtain a polymer of sufficient uniformity to be useful.

In a bifunctional (linear) polymerization, there is no propagation between growing chains, and high molecular weights of a hundred thousand or greater are readily attained. During the course of a given addition polymerization reaction, the average molecular weight of the polymer chains remains practically the same; however, the polymer yield (i.e., the ratio of polymer to monomer) continues to increase, and the viscosity of the monomer-polymer mixture continues to rise, until all the monomer is consumed. Because of the great chain length of addition-type polymers, the presence of even small amounts of polyfunctional substances quickly produces a rigid, crosslinked, insoluble polymer.

3.1.2.3. CONDENSATION POLYMERIZATION.— Condensation polymers are formed through the chemical combination of reactive groups of bifunctional or polyfunctional molecules, with the splitting out of a small molecule, usually water, as a by-product. Either linear or crosslinked polymers may be formed, depending on whether the functionality of the reacting molecules is 2 or greater than 2. The reactive groups that take part in polycondensation reactions are the same as those (e.g., hydroxyl, carboxyl, amino, etc.) that take part in the ordinary condensation reactions between small molecules, as for example when an alcohol and an organic acid react to form an ester.

A polycondensation reaction proceeds at the same characteristic rate as the reaction between similar groups in a monofunctional reaction. Unlike addition polymers in which long chains form rapidly by a free radical propagation mechanism, condensation polymers have a reaction activation energy that requires time and heat for the formation of long chains. The polycondensation reaction proceeds randomly among all functional groups, whether they are on a monomer molecule or on a short or a long polymer chain. That is, reactions between partly grown chains, between a growing chain and a monomer molecule, and between two monomer molecules are all equally probable. Consequently, the monomer molecules are soon consumed in the production of dimer, trimers, and short polymer chains. The reaction mixture now consists largely of low molecular weight polymer chains which continue to grow by combining with each other for as long as they are permitted, or until the viscosity of the mixture increases to an extent that limits the mobility of reactive groups and becomes the rate-determining factor in further polymerization.

Even when polycondensation reactions are forced to completion, molecular weights higher than 25,000 are seldom obtained. However, if the reacting substances are polyfunctional, then cross-linking reactions between even relatively low molecular weight chains will soon build up a three-dimensional structure and lead to gelation and polymer insolubility.

3.1.3. Methods of Polymerization

Four different methods of polymerization are in general use: bulk, solution, emulsion, and suspension. Each process is briefly discussed below.

3.1.3.1. BULK POLYMERIZATION.—This is the simplest type of polymerization process, since the reaction mixture consists of a single phase with nothing usually added, except catalyst or initiator if required. Thus the polymerized product is obtained in an inherently pure chemical state that eliminates the need for subsequent purification steps. However, the bulk process is difficult to control from the standpoint of obtaining a product of reasonably uniform molecular weight and density. The reaction mixture soon becomes very viscous, causing difficulties in agitation and heat removal. Since most polymerizations are exothermic (addition polymers, in particular, usually have a high exotherm), local variations in temperature and extent of reaction occur, and the final product may vary considerably throughout the polymerized mass. The high viscosities encountered in bulk polymerizations often limit the degree of conversion that can be obtained within a reasonable length of time. The bulk method is used chiefly for cast plastics and for *in situ* polymerizations in which the time element is relatively unimportant, so that a slow but controllable reaction (perhaps at low temperature) is feasible.

3.1.3.2. SOLUTION POLYMERIZATION.—In the solution process, the monomeric substances (with added catalyst or initiator if required) are dissolved in an inert liquid which may or may not be a solvent for the polymer. If the polymer is insoluble in the liquid, it precipitates out as it forms. Otherwise, when the polymerization has proceeded to the extent desired, the polymer is recovered by precipitating it with a suitable nonsolvent, or less often by evaporating off the solvent and residual monomer.

The solution polymerization process is more easily controlled than the bulk process, and a more uniform product is obtained. The lower viscosity and better heat transfer properties of the solution medium permit easier agitation with better control of temperature and a more uniform reaction mixture. Although applicable to either addition or condensation polymerizations, the solution method is particularly well-suited for the condensation type of reaction. Alkyds, phenolics, epoxies, and many other condensation polymers are prepared by the solution method.

3.1.3.3. EMULSION POLYMERIZATION.—In the emulsion process, the monomer (which is insoluble in water) is emulsified in water with the aid of suitable emulsifying agents. The method is used almost exclusively for addition polymerizations, since the moderate or low temperatures employed are unsuitable for most condensation reactions. The polymerization proceeds very rapidly in the presence of an initiator, yielding a high molecular weight product in finely divided form. Excellent control of the process is possible, and a very uniform polymer is obtained. Since the polymer is obtained in the dispersed phase, there is no appreciable increase in the viscosity of the reaction mixture as the polymerization proceeds. Many difficult polymerizations and copolymerizations that take place very slowly or not at all by bulk or solution methods are readily carried out by the emulsion method. The economy and nonflammability of the aqueous dispersion medium are also distinct processing advantages.

The very small particle size and good uniformity of emulsion polymers permits their use (after removal of processing agents where necessary) directly in the manufacture of latex paints, plastisols (vinyl dispersion resins), and special molding powders.

3.1.3.4. SUSPENSION POLYMERIZATION.—This is the newest method of polymerization. The polymer is obtained in the form of tiny beads or pearls that are readily washed free of processing contaminations. The suspension polymerization process is somewhat similar to an emulsion system in that there is a dispersed phase and a dispersion medium, usually water. However, no emulsifying agent is used and an emulsion does not exist. Instead, monomer droplets (much larger than those in an emulsion system) are mechanically dispersed in the water medium by vigorous agitation. The droplets remain suspended only so long as the agitation continues. A suitable suspension agent (e.g., an insoluble inorganic salt or oxide, or a soluble organic polymer) is usually used to prevent the coalescence of partly polymerized particles and to help control the particle size developed.

The mechanism of suspension polymerization is analogous to that of the bulk method rather than the emulsion method. Each monomer droplet or bead acts, in effect, as a small, discrete bulk polymerization system. Hence, only those substances capable of bulk polymerization can be polymerized by the suspension method. However, whereas the bulk process is very difficult to control, excellent control of the suspension polymerization process is possible. As in the emulsion method, there is virtually no increase in the viscosity of the reaction mixture with polymerization. The moderate or low temperatures employed are readily maintained throughout the thoroughly agitated reaction mixture, and a very uniform polymer is obtained. Again, the economy and nonflammability of the water dispersion medium are important processing advantages. The suspension method, like the emulsion method, is used primarily for addition polymerizations.

3.1.4. Types of Polymers

The complexity and diversity of chemical composition and physical structure among the many synthetic polymers that have become available has resulted in a growing descriptive nomenclature by which to classify them. Besides the broad distinctions already made in the preceding sections, such as addition or condensation polymers, linear or cross-linked, thermoplastic or thermosetting, etc., we may now consider, from the point of view of structure, types of addition polymers variously described as homopolymers, copolymers, heteropolymers, and stereo-regular polymers. A familiarity with the basic structure and properties of the materials described by these terms will be of value to those in the coatings field who are interested in the potential usefulness of recent types of polymers.

3.1.4.1. A HOMOPOLYMER is formed from a single monomer, so that all the structural repeating units in every chain are identical. All the polymer chains are therefore similar in chemical composition, but they may vary in chain length and structure (and in the associated physical properties), depending on the degree and type of process control that has been exercised. Typical homopolymers are polystyrene and poly(methyl methacrylate).

3.1.4.2. A COPOLYMER is formed from two (or more) different monomers. The definition of copolymer sometimes includes the stipulation that each of the constituent monomers must be capable of undergoing polymerization by itself. In this school of thought, if one (or more) of the monomeric constituents is itself incapable of polymerization (although it will polymerize in the presence of the other, true monomer), then the resulting polymer is termed a HETEROPOLYMER. The author believes that the distinction made between "copolymer" and "heteropolymer" tends to create more confusion than order, and finds that the term "heteropolymer" is not favored in the writings of most leaders in the high polymer field.

In ordinary copolymers, the comonomers are combined into the polymer chain randomly rather than in a regular sequence, so that different chains vary in chemical composition as well as in length and structure. Practically, however, it is the average composition that

largely determines the bulk properties of the polymer produced. The average copolymer composition may be expressed in terms of the over-all ratio of one component to the other, and it depends on the relative amounts and reactivities of the comonomers present in the reaction mixture. To achieve a uniform average composition throughout a particular copolymerization, it is necessary to add appropriate amounts of the faster reacting monomer as the reaction progresses in order to maintain the original reaction environment.

Through copolymerization it is possible to obtain polymers with properties intermediate between those of the individual homopolymers. Homopolymers that cannot be mechanically blended because of incompatibility often have compatible monomers that can be successfully combined through copolymerization. It should be pointed out, however, that the properties of a copolymer may be very different from those of a physical mixture of the two homopolymers in the same proportion. For instance, a random copolymer, under any given set of conditions, behaves as a single compositional entity, whereas each component in the physical mixture may "go its own way."

A good example of copolymerization is that of vinyl chloride and vinyl acetate. Vinyl chloride alone forms a hard, horny, difficultly soluble homopolymer, while vinyl acetate alone forms a soft, tacky, easily-soluble homopolymer. Copolymerization of the two monomers in various ratios yields a series of copolymer resins with highly useful intermediate chemical and physical properties (see sec. 3.6.3).

3.1.4.3. A BLOCK POLYMER is a special type of copolymer in which the different monomeric repeating units, instead of occurring randomly along the polymer chain as in ordinary copolymers, occur in relatively long sequences (blocks) of one constituent alternating with relatively long sequences of the other. The alternating runs or blocks of each repeating unit may be of varying length and are usually linked together in linear fashion (although the possibility of making crosslinked block polymers, through the use of polyfunctional monomers, exists).

Because they contain long runs of each constituent monomer, block copolymers tend to exhibit the chemical properties of each constituent rather than a single set of intermediate properties as in random copolymers, where the closer alternations of the different monomeric units impart a pseudo-homogeneous character to the polymer. Thus, a random copolymer of a hydrophobic and a hydrophilic monomer would ordinarily exhibit an intermediate, lessened hydrophobic or hydrophilic character, depending on the average monomer ratio; for example, it might have only limited solubility in a few organic solvents and be virtually insoluble in water. The block copolymer of a hydrophobic and a hydrophilic monomer, on the other hand, would tend to have a dual character and show solubility in both organic and aqueous media. Such a block polymer would be expected to make a good emulsifying agent. Block copolymers can be prepared either by addition polymerization (e.g., poly(ethylene-propylene oxide)) or by a polycondensation reaction (e.g., epoxy-phenolic copolymer).

3.1.4.4. A GRAFT POLYMER is a special type of branched copolymer consisting of a linear main chain of one monomeric repeating unit with side chains of another. It is made by grafting side chains composed of one polymeric species onto a main chain of another polymeric species. Since each copolymer molecule thus has a distinctly dual structural character, graft polymers (like the block polymers described above) tend to exhibit the properties of each polymeric constituent rather than a single set of intermediate properties.

Graft copolymers are prepared by dissolving the already polymerized main polymer in the monomer to be grafted onto it. The grafting reaction usually proceeds by an addition process at active sites (double bonds, free radicals, etc.) activated or induced by heat, catalysis, or radiation. Graft polymers that have been successfully prepared include grafts of vinyl acetate onto poly(vinyl alcohol), polyethylene onto poly(vinyl acetate), and styrene onto butadiene-styrene copolymer.

3.1.4.5. STEREOREGULAR POLYMERS are a recent development in linear, addition polymers that followed the discovery of solid, heterogeneous-type catalysts capable of exerting a highly stereospecific effect on the polymerization of olefin-type monomers, such as ethylene and propylene. It is thought that the catalyst, through a highly specific selectivity for particular isomeric forms, activates only certain sites in the monomer molecule in a manner that leads to an orderly polymerization in which the monomer molecule always adds to the growing chain in the same steric configuration. The resulting polymer chains have a predetermined, regular structure that permits close packing with formation of a high-density, crystalline polymer. Such a polymer possesses a higher softening point, greater mechanical strength, and greater chemical resistance than the analogous amorphous polymer (see sec. 3.13.1 on Polyethylene).

3.1.5. Classification of Synthetic Resins

Synthetic resins may be classified in various ways: according to chemical or structural type, manner of formation, properties, applications, or other criteria, depending on the objective to

be served. Categories such as condensation and addition polymers, thermoplastic and thermosetting resins, linear and cross-linked substances, etc. were discussed in the preceding section. Such information is of basic usefulness in understanding the nature of synthetic resins and the relationships between their composition, structure, and properties. It is necessary now to consider these materials from the point of view of their selection for coatings applications. For this purpose they will be discussed under headings that refer to the commonly accepted designations for these classes of resins. Broad structural generalizations that would lead us, for example, to classify polystyrene, acrylic, and other familiar resins as vinyl polymers will be avoided.

Only the main types of resins that are important or promising for coatings applications can be discussed in the space available. It should be borne in mind that, in general, a combination of resins will yield a material with intermediate or combined properties. These properties may be further altered upon formulation of the resin into a coating material. The ultimate properties of the coating are determined also by the manner in which the film is deposited and cured. Thus an almost infinite variety of coatings formulations and properties

are possible even with only a limited number of basic resins. Nevertheless, it is possible to predict much about the properties and potential performance of a given coating material from a knowledge of the properties of the basic ingredients, particularly the film-former, of which it is composed.

The following main classes of synthetic resins are discussed in the sections of this chapter designated below:

3.2. Cellulose Derivatives

The chief sources of cellulose for the manufacture of "cellulosic" coating materials are wood, cotton, and cotton linters. Although cellulose itself is insoluble except in a few specialized reagents (e.g., cuprammonium solution), it can be converted by suitable chemical treatment, involving esterification or etherification of the hydroxyl groups with or without subsequent hydrolysis, into a variety of useful, soluble cellulose derivatives, including cellulose esters, cellulose mixed esters, and cellulose ethers. Through control of the degree of substitution (esterification or etherification) and of the processes of hydrolysis and degradation, the chemical composition and the molecular weight of the cellulose derivative can be controlled to give the desired solubility, viscosity, and mechanical, physical and chemical properties.

The most important and widely used cellulose derivatives are the esters, particularly cellulose nitrate and cellulose acetate. Cellulose acetate-butyrate is the most widely used mixed ester and finds important use in the coatings field. Ethyl cellulose is the most widely used of the cellulose ethers.

The cellulose derivatives are thermoplastic materials and therefore are permanently soluble and heat-softenable. The different cellulose derivatives differ considerably in their solubil-

ity in particular solvents and in their softening temperatures, depending on chemical type, degree of hydroxyl substitution, molecular weight and viscosity. Some are widely soluble in organic solvents, others only in water. Softening points may range from about 285 to 570 °F (about 140 to 300 °C). Cellulose nitrate is an exception in that it decomposes (sometimes with explosive violence) when heated, before reaching a melting temperature.

The cellulose derivatives, being thermoplastic, form films from solution by simple evaporation of solvent. As a group, they are tough, horny materials that must be plasticized to achieve adequate flexibility and adhesion for coating purposes. They are fast drying because they release easily the quick-evaporating liquids in which they are soluble. It should be noted, however, that both diluents and higher-boiling solvents are used along with the low-boiling active solvents in their formulation into lacquers, to control the evaporation rate and solution viscosity (see sec. 5.3.2 on Use of Thinners).

3.2.1. Cellulose Esters

3.2.1.1. CELLULOSE NITRATE (or nitrocellulose, as it is often but incorrectly called) is the oldest of the cellulose derivatives, its preparation having been reported by Bracconot [44]

in 1833. It was not until 1923, however, that a cellulose nitrate lacquer was developed with the durability and fast-drying qualities that revolutionized the automobile finishing industry by cutting the finishing time from weeks to hours. Shortly thereafter, the furniture industry adopted cellulose nitrate lacquers, and soon its use had spread to a wide variety of products. To this day, as the film-forming base in most quick-drying lacquers, and as a versatile material that is widely compatible with other resins, oils, and plasticizers, cellulose nitrate is extensively used in the coatings field.

Cellulose nitrate is produced by the nitration of purified cellulose with a mixture of nitric and sulfuric acids. The degree of nitration obtained is determined largely by the ratio of the mixed acids. The fully nitrated product (containing 14.14 percent nitrogen) is insoluble and unstable. Soluble cellulose nitrate for coatings purposes [45] usually has a nitrogen content between 11.5 and 12.2 percent. The solubility also depends on the molecular weight or viscosity of the cellulose ester. Although strength and durability improve with increasing molecular weight and increasing viscosity, the solubility becomes poorer. To secure the good solubility and low solution viscosity needed for practical high-solids coatings formulations, the cellulose nitrate as first produced is subjected to controlled degradation by digestion in water under heat and pressure until the molecular weight has been reduced to the desired value. Thus the viscosities of commercial cellulose nitrates represent a compromise (as with many processes) between the conflicting requirements of product formulation and product performance. Both nitrogen content and viscosity must be controlled within fairly narrow limits to yield a material that is sufficiently uniform for coatings formulation; otherwise, less soluble portions may not dissolve completely, while very low molecular weight portions may reduce tensile strength. To obtain a material of specified average viscosity, it is common practice to blend different batches of cellulose nitrate that are not too widely apart in this property.

Cellulose nitrate itself is a tough, horny material that soon discolors, embrittles, and decomposes on exposure to heat or sunlight. However, when compounded with suitable plasticizers, resins, stabilizers, and pigments in a properly formulated solvent vehicle it yields a very wide variety of useful and durable coating materials. Cellulose nitrate is soluble in esters, ketones, nitrohydrocarbons, and ether-alcohols. Alcohols alone swell and soften it but do not dissolve it (an exception is a special alcohol-soluble grade containing 10.7 percent nitrogen). It is insoluble in aliphatic and aromatic hydrocarbons but will tolerate large proportions of these diluents in the presence of suitable active solvents. It has very good mois-ture resistance and dimensional stability. It is resistant to weak acids and alkalis but is decomposed by strong ones.

Pure, dry cellulose nitrate is a dangerously flammable material. It is therefore handled and shipped only in a wet state. For shipping, it is usually wet with alcohol as 30–35 percent of the total weight. After compounding with other ingredients, the flammability of the final film is greatly reduced but still high compared to other film-forming substances.

Although cellulose nitrate is available in viscosity grades ranging from about 0.05 second (20 centipoises) to 1000 seconds or more [45], the majority of lacquers utilize a $\frac{1}{4}$-second or a $\frac{1}{2}$-second material as a good compromise between tensile strength and solubility requirements. For airplane dopes, where extra tensile strength and the fabric-tautening property are necessary, cellulose nitrate of higher viscosity (5–20 seconds) has been found to give the best results, as reflected in Government specifications for such materials [45, 46].

While cellulose nitrate has been combined with many different resins to produce useful coatings, perhaps the most outstanding have been those in combination with alkyd and amino resins to produce tough, hard, durable lacquers capable of withstanding the severe service requirements of automotive, aircraft, and other industrial finishes. Successful coatings have also been based on blends of cellulose nitrate with natural resins and drying oils, resin derivatives, phenolic resins, acrylic resins [138], certain vinyl resins, and others. Applications include coatings for metal, wood, paper, fabrics, leather, and cellophane. These are available in a wide variety of colors and surface textures. A recent successful application for cellulose nitrate has been as the film-forming base in multi-color finishes (see sec. 2.3.7).

3.2.1.2. CELLULOSE ACETATE, although used in large quantities in the plastics and textiles fields, finds only limited use in the coatings field because of its poor solubility in many commonly used organic solvents, its limited compatibility with plasticizers and resins, and its relatively high moisture absorption which results in poor dimensional stability. However, it is resistant to discoloration and degradation by heat and ultraviolet light, has a high softening temperature (approximately 446 to 572 °F [230-300 °C], depending on the composition and molecular weight), and is relatively slow-burning.

Cellulose acetate is manufactured by acetylating cellulose with acetic anhydride and glacial acetic acid in the presence of sulfuric acid as a catalyst. The fully acetylated material (cellulose triacetate) thus obtained is virtually insoluble except in chloroform and a very few other solvents. It is therefore partially hydro-

lyzed to yield more soluble materials of wider usefulness. Various commercial grades are available for particular applications. These differ in degree of hydrolysis (or esterification), molecular weight, and viscosity; therefore, they differ in solubility, softening point, tensile strength, and other properties.

Solvents useful with cellulose acetate include acetone, methyl ethyl ketone, methyl acetate, ethyl acetate, dioxane, and the glycol-ethers. Methyl alcohol and ethyl alcohol are good co-solvents in combination with methylene chloride, ethylene dichloride, nitromethane, and 1-nitropropane. The number of plasticizers useful with cellulose acetate is very limited, and a careful choice for particular applications is necessary. Methyl- and ethyl phthalyl ethyl glycollate are generally useful, and a few phthalates, phosphates, and citrates are of limited usefulness as plasticizers. Among the few resins with which cellulose acetate is fairly compatible are certain phenolics, alkyds, and ester gums.

Cellulose acetate is resistant to everyday chemicals such as dilute acids, animal fats, vegetable and mineral oils, gasoline, and ethyl alcohol. It is decomposed by strong acids and by alkalis. It is used in lacquers for paper, fabrics, wood, metal and wire, particularly where good resistance to heat and light is required.

3.2.1.3. CELLULOSE PROPIONATE is prepared by the esterification of cellulose with propionic anhydride, in a manner similar to the preparation of cellulose acetate. The larger propionyl radical yields a softer, lower-melting material than does the acetyl radical. Cellulose propionate is more soluble and requires much less plasticization than the corresponding acetate. It is tough, shock-resistant, heat-stable, and weather-resistant. It has only recently become commercially available. Although at present used chiefly as a plastics molding powder, it has found some application in strippable coatings (sec. 2.2.7) and gel lacquers [158].

3.2.1.4. CELLULOSE BUTYRATE can be made by processes analagous to those for the acetate and the propionate. The bulkier butyryl radical results in a still softer, lower-melting, and more soluble material that is not in itself very useful. However, the properties of the butyryl radical have been utilized to excellent advantage in the coatings field by combining butyryl with acetyl in the manner described under Cellulose Mixed Esters.

3.2.2. Cellulose Mixed Esters

By esterifying cellulose with a mixture of acetic and propionic or butyric anhydrides, mixed esters can be made that combine many of the most desirable properties of each constituent. The ratio of acetyl to propionyl or to butyryl can be varied and the degree of esterification (or hydrolysis) can be controlled to produce a wide range of materials. As with other polymeric materials, the physical and mechanical properties also depend on molecular weight and viscosity.

3.2.2.1. CELLULOSE ACETATE-BUTYRATE combines the good light and heat resistance of cellulose acetate with the better moisture resistance and dimensional stability of the butyrate. The butyryl radical imparts to the mixed ester greater flexibility, better solubility, and wider compatibility than is obtainable with the acetate alone. Cellulose acetate-butyrate requires much less plasticization than cellulose acetate and is compatible with a much broader range of plasticizers and resins. It is soluble in ketones, esters, chlorinated hydrocarbons, and nitrohydrocarbons. Alcohols and aromatic hydrocarbons are well-tolerated diluents. Because of its versatility of composition, moisture resistance, dimensional stability, and weathering resistance, cellulose acetate butyrate finds considerable use in both clear and pigmented lacquers for metal, wire, paper, plastics, wood and fabrics. Its slow-burning characteristics combined with good tensile and tautening properties and excellent outdoor durability have been the basis for its use by the Navy and Air Force as a dope [47, 48, 49] for the fabric surfaces of military aircraft (training planes and slower transport planes) in place of the hazardously flammable cellulose nitrate dope. Cellulose acetate butyrate has been notably successful in the formulation of strippable coatings, hot melt lacquers, and gel lacquers [158].

3.2.2.2. CELLULOSE ACETATE-PROPIONATE, although its utility as a film-forming base has been established through a comprehensive study [50], has been used to only a limited extent in the coatings field. This is largely because of the earlier and adequate availability of cellulose acetate-butyrate, and the similarity in properties of the two mixed esters, which has made it uneconomic to manufacture the acetate-propionate on a large scale.

3.2.3. Cellulose Ethers

In general, cellulose ethers are prepared by treating alkali cellulose with an appropriate etherifying agent, usually an alkyl chloride, under heat and pressure. By control of the reaction conditions, it is possible to control the degree of substitution and the viscosity, upon which the physical and chemical properties of the cellulose ether depend.

3.2.3.1. ETHYL CELLULOSE finds extensive use in the coatings field [51]. It is tough, flexible

at low temperatures, and stable to heat, light, and weathering, particularly when properly plasticized and stabilized. Its wide compatibility with plasticizers, resins, gums, and waxes permits an almost endless variety of useful formulations. It is completely compatible with cellulose nitrate and is often used to augment the properties of cellulose nitrate lacquers [52]. Though widely soluble in organic solvents, ethyl cellulose is resistant to alkalis, dilute acids, and aliphatic hydrocarbons. Although somewhat permeable to water vapor, it is low in water absorption and has good dimensional stability. Its electrical properties (insulative, dielectric, etc.) are excellent.

Ethyl cellulose is used extensively in coatings for wire, paper, fabric, leather, and plastics. It is also used in coatings for metal, wood, glass, and ceramics. Hot-melt strippable coatings (sec. 2.2.7) for metal parts are readily formulated with ethyl cellulose.

3.2.3.2. METHYL CELLULOSE can be produced with a wide range of solubility properties, from solubility in alkalis to solubility in organic solvents, depending on the degree of methylation. However, the usual commercial product has a degree of substitution of about 2 and is soluble in cold water but not in hot. The water soluble product has very poor acid and alkali resistance but is insoluble in organic solvents and has excellent resistance to oils and greases. An important use has been as a grease-proof coating for paper. Methyl cellulose is used extensively as a thickening agent and protective colloid in emulsion paints and as a thickener in paint removers.

3.2.3.3. CARBOXYMETHYL CELLULOSE as usually manufactured is a water-soluble cellulose ether that is insoluble in organic solvents. It has poor resistance to acids and alkalis. Its aqueous solutions are highly viscous, making it a useful thickening and stabilizing agent for latex paints. It finds some use also as a fabric finishing agent and as a grease-proofing coating for paper, leather, and other materials.

3.2.3.4. HYDROXYETHYL CELLULOSE, as usually prepared, is a water soluble product. It is very resistant to organic solvents, oils, and greases. It has fair resistance to dilute acids and alkalis. It finds some use in coatings for paper, fabrics, and leather where a grease-proof or water-soluble coating is desired. Its chief use in the coatings field is as a protective colloid in latex polymerization and as a thickening agent and stabilizer for latex paints.

3.2.3.5. BENZYL CELLULOSE resembles ethyl cellulose in general properties but is softer and lower in melting point because of its bulkier molecular structure. It is widely soluble in organic solvents and is compatible with most common resins and plasticizers. However, it has found only limited use in the United States, where ethyl cellulose has met with far more favor. The chief uses for benzyl cellulose are in chemical-resistant coatings and electrical insulating coatings.

3.3. Phenolic Resins

Phenolic resins were the first truly synthetic resins to become commercially available. They were introduced to the coatings field by Baekeland about 1909 [53]. Their characteristic fast dry, moisture resistance, toughness, and durability, and their reasonable cost have led to their wide use in coatings.

Phenolic resins are made by the condensation of a phenol with an aldehyde. A variety of types is available, depending on the nature and proportions of the phenol and aldehyde, the type of catalyst employed, and the reaction conditions. Formaldehyde, because of its high reactivity and low cost, is by far the most used aldehyde. Besides phenol itself, many substituted phenols have been of wide commercial importance. Both heat-reactive and non-heat-reactive types of phenolic resins are available. Heat-reactivity, with the associated capability for cross-linking and insolubilization, is favored by high proportions of formaldehyde and by alkaline catalysts. Acid catalysts generally yield thermoplastic resins (novolacs) that are permanently fusible and soluble, although a high formaldehyde ratio can impart cross-linking characteristics to these resins also.

Phenolic resins have a yellow color which tends to darken on aging; hence they are not usually employed in white finishes. The darkening tendency is greatest with the resin-modified phenolics and least with the para-substituted pure phenolics. In general, phenolic resins have good resistance to acids and to weak bases but poor resistance to strong alkalis. For use as coatings under the weakly alkaline conditions encountered in ordinary environments and on common alkaline surfaces such as plaster or concrete, phenolic resins are very satisfactory.

Phenolic resins used in the coatings field may be classified on the basis of their composition and properties into the following main categories:

(1) Modified phenolic resins, oil-soluble
(2) Pure phenolic resins (100% phenolic)
    a. Oil-soluble, thermoplastic
    b. Oil-soluble, heat-reactive
    c. Alcohol-soluble, oil-insoluble, thermosetting
(3) Phenolic dispersion resins.

Each of the above types is briefly discussed in the sections which follow.

3.3.1. Modified Phenolic Resins, Oil-Soluble

The first phenolic resins used in the coatings field were of the modified phenol-formaldehyde type, the usual modifier being rosin or its glyceryl ester (ester gum). The modification was necessary to render the phenol-formaldehyde resin soluble in drying oils. The use of these modified phenolic resins in varnishes in place of the natural resins, ester gum, maleic and other resins used up to that time resulted in varnishes with much faster drying properties and greatly improved water and alkali resistance and durability. Other phenolic resins rendered oil-soluble by modification are those based on *m*-cresol and 3,5-xylenol. It may be noted that, as a rule, it is the meta-substituted phenol derivatives that must be modified to render them oil-soluble.

Though not as highly resistant and durable as the pure phenolic resins that were developed later, modified phenolic resins are lower in cost, have better adhesion properties, and are very well-suited for many important coating applications. They are widely used for interior applications where fast drying, water and alkali resistance, and durability are essential, as in furniture finishes and floor varnishes. They make good primer-sealers for plaster and wood. They find considerable use in long-oil exterior coatings such as spar varnishes, and porch and deck enamels, and in short-oil, fast-drying, traffic paints. As already mentioned, modified phenolics are not ordinarily used in white finishes because of their strong yellowing tendency. Their electrical properties (insulative, dielectric, etc.) are poor.

In addition to being very useful in themselves, modified phenolic resins are of general usefulness in upgrading the drying speed, water resistance, and durability of lower cost coating materials. Also, they are frequently used to improve the adhesion properties of the otherwise superior pure phenolic resins.

3.3.2. Pure Phenolic Resins (100% Phenolic)

Pure phenolic resins (or 100% phenolic resins, as they are often called) are among the most chemical-resistant and durable resins in the coatings field. They have been available since about 1928. The oil-soluble types are made by the condensation of para-substituted phenols with formaldehyde. Occupation of the highly reactive para position by the substituent group reduces the reactivity (and crosslinking tendency) of the molecule sufficiently to render it soluble in drying oils without rosin modification. These oil-soluble phenolic resins may be either thermoplastic or heat-hardening types. Alternatively, by using other phenols and suitable phenol-formaldehyde ratios and appropriate catalysts, oil-insoluble but alcohol-soluble resins can be formed which are completely thermosetting. The pure phenolic resins as a group are characterized by excellent exterior durability and outstanding water, solvent, and chemical resistance. Although better than the modified phenolics in color stability, they still tend to yellow and hence are not usually used in white finishes. Another limitation is their relatively poor adhesion; this is usually overcome by combining them with small portions of a modified phenolic. Drying properties range from slow to very fast, with most of the pure phenolics in a fast-drying category.

3.3.2.1. OIL-SOLUBLE, THERMOPLASTIC, pure phenolic resins are made by condensing approximately equimolar proportions of a para-substituted phenol with formaldehyde in the presence of an acid catalyst. This is the type of phenolic resin most used in air-drying varnishes and oleoresinous paints. Such a resin is covered by Fed. Spec. TT–R–271 [119]. Such phenolic varnishes [135, 137] and paints have excellent outdoor durability and are used extensively in structural and marine applications such as bridges, locks and dams, and storage tanks. They find use also as exterior trim paints, automotive primers, and appliance coatings. Some of the finest exterior spar varnishes are made with this oil-soluble, thermoplastic type of pure phenolic resin. (For more information on phenolic paints and varnishes, see sec. 2.3.2.2.)

3.3.2.2. OIL-SOLUBLE, HEAT-REACTIVE, pure phenolic resins are made by condensing a para-substituted phenol with formaldehyde in the presence of an alkaline catalyst, using a higher proportion of formaldehyde (about 2 moles of formaldehyde to one mole of substituted phenol) than is used in making the thermoplastic resins. The condensation reaction is interrupted at an intermediate stage at which the resinous condensate is still oil-soluble though reactive. The partly polymerized resin is subsequently heat-reacted with drying oils to produce varnishes with very rapid bodying properties. Short-oil industrial baking varnishes of this type make excellent insulating and impregnating varnishes for electrical equipment because of their fast, deep-curing characteristics and their excellent insulative and dielectric properties. Even small proportions of an oil-soluble, heat-reactive type of pure phenolic resin have a marked effect in increasing the drying speed, water resistance, hardness, and durability of other, lower grade resin formulations. This "upgrading" function is an important use for this type of phenolic resin.

3.3.2.3. ALCOHOL-SOLUBLE, OIL-INSOLUBLE, THERMOSETTING, pure phenolic resins are based on phenols other than the oil-soluble para-substituted types. The condensation reaction between the oil-insoluble phenol (usually a meta-substituted phenol or phenol itself) and formaldehyde is carried out in alkaline solution at a fairly high formaldehyde ratio that imparts a high degree of reactivity to the resulting resin. The reaction is stopped at an intermediate stage of polymerization while the resin is still alcohol-soluble and reactive. The partially polymerized resin is supplied as a solution in an organic solvent. The applied coating, when heated, converts to a completely polymerized, thermoset, insoluble resin film that is highly resistant to corrosion, abrasion, and chemical attack.

In resistance and durability, the alcohol-soluble, thermosetting phenolic resins are superior to other types of pure phenolic resin. The completely thermoset resin is highly resistant to organic solvents, organic acids, mineral acids (except strong oxidizing acids such as nitric), and atmospheric corrosion. Special types resistant even to strong alkali also are available. The thermosetting phenolics may be cured at room temperature by adding amine-type or other alkaline catalysts; however, maximum chemical and solvent resistance is obtained with heat curing.

Extensive use is made of the thermosetting pure phenolic resins in coatings for the insides of cans, drums, and tanks carrying organic solvents, foodstuffs, and chemicals. They find wide use on military equipment [125, 136] such as ammunition boxes, aircraft parts, water and gasoline tanks, and food containers. They are used for steel structures and fabricated parts subject to severe atmospheric exposure. And they have proved durable as coatings for submerged steel parts and for buried iron pipe.

3.3.3. Phenolic Dispersion Resins

Phenolic dispersion resins are highly polymerized phenolic resin-oil complexes dispersed in volatile organic solvents. They are non-oxidizing and dry quickly by evaporation of solvent to form highly weather-resistant films that have a high degree of impermeability to moisture, excellent resistance to water and dilute alkali, good adhesion to metals, and good resistance to strong solvents such as alcohols, ketones, esters, and ethers. Because of their resistance to such solvents, they make good non-lifting primers under lacquers based on vinyls and on cellulose derivatives. Although useable alone, they are usually blended with an alkyd or other varnish resin. The military specification for zinc chromate primer for aircraft use [54] calls for a vehicle based on a phenolic dispersion resin blended with an alkyd resin. Phenolic dispersion resins find use in quick-drying industrial primers and undercoats, as shop coats for structural and fabricated steel parts, in traffic paints where they contribute fast dry and durability, in deck and floor coatings, and in sealers for wood, paper, and wallboard.

3.4. Alkyd Resins

Alkyds are the most important and most widely used resins in the coatings field. In versatility of formulation and application, in overall economy, and in general durability, they are unexcelled. They have been aptly characterized as "the work-horse of the coatings industry". Alkyd resins have been available commercially since 1927.

3.4.1. Composition and Properties of Alkyd Resins

3.4.1.1. AN ALKYD is a synthetic resin made by the esterification of a polyhydric alcohol with a polybasic acid. Although a wide variety of resinous products of polyhydric alcohols and polybasic acids is included in the general term "alkyd", the most important group (and the type generally meant when speaking, without other qualification, of an alkyd resin) are the oil-modified glyceryl phthalate resins. These are the reaction products of glycerol and phthalic anhydride (phthalic acid), modified with either drying, semi-drying, or non-drying oils (see sec. 2.2.1). Pentaerythritol is the most important of the lesser used polyhydric alcohols; it yields resins that are faster setting and more durable than glyceryl alkyds, but which are more expensive to manufacture and formulate. Isophthalic, maleic, sebacic, and other polybasic acids also find use in alkyd resin manufacture. Long chain dibasic acids, such as sebacic or adipic acids, yield soft resins that make good polymeric plasticizers for harder materials.

The unmodified glyceryl phthalate resin is a hard, brittle solid of only limited solubility. Through reaction with fatty acids or oils at the time the alkyd resin itself is being formed in the cooking kettle, a series of modified alkyd resins having a wide range of specific desired properties intermediate between those of the resin and the oil can be produced. The resin can be prepared by either bulk or solution polymerization methods (see sec. 3.1.3). In either case the cooking or refluxing is continued until the viscosity and acid number of the reaction mixture reach a predetermined value (when the

resin is close to the gel stage), whereupon the mixture is quickly cooled to stop the reaction. The resin is usually supplied as a solution in an organic solvent. Long-oil alkyd resins are soluble in mineral spirits; short-oil alkyds require stronger solvents such as xylene or other aromatic solvents; the unmodified resin is soluble only in strong solvents such as ketones and esters and other oxygenated solvents. Several types of long- and medium-oil alkyd resins are covered by Fed. Spec. TT–R–266 [120].

Oil-alkyds may be further modified with a variety of other resins to achieve certain properties. In general, most of these doubly-modified resins (amino resins excepted) tend to have a darker color than the straight oil-alkyd. Some resins can be incorporated into the alkyd during the original cooking process; for example, a modified natural resin like congo ester to impart faster drying properties, or a rosin-modified phenolic resin to improve water and alkali resistance—although the exterior durability may be lessened by such modification. Or the alkyd, particularly non-drying types, may be physically blended with tough resins such as a vinyl chloride-acetate [55] or cellulose nitrate [52] to plasticize them and to improve their gloss and chalk resistance. Alkyds may also be chemically combined with reactive monomers such as styrene or a silicone to obtain copolymers with intermediate properties. Non-drying (non-oxidizing) alkyds can be cured to exceptionally durable films by baking with amino resins (sec. 3.5) such as urea- or melamine formaldehyde. The air-drying alkyds require the use of metallic driers as used in ordinary drying oil paints in order to dry properly within a reasonable length of time.

3.4.1.2. EFFECT OF OIL-MODIFICATION.—Oil-modified alkyd resins may be either air-drying or baking types, drying or non-drying (oxidizing or non-oxidizing), yellowing or non-yellowing, weather- or chemical-resistant, flexible or hard, etc., depending on the type of oil and the oil length. Drying, semi-drying, and non-drying oils (see sec. 2.2.1) may be used, singly or together, in either long, medium or short oil lengths. The best air-drying properties are obtained with long oil alkyds made with good drying oils such as linseed and dehydrated castor, although air-drying alkyds of medium oil length also are available. The palest color and best color-retention are obtained with non-drying oils such as cocoanut and castor; however, these non-drying alkyds must be blended or baked with a film-forming resin (e.g., ethyl cellulose or urea-formaldehyde) in order to form a suitable film. Excellent intermediate drying and color-retention properties are achieved by use of a semi-drying oil such as soybean or safflower; soybean oil, in particular, is very

widely used in alkyd resin modification because of its good non-yellowing properties, ready availability, and low cost. Good brushability, surface wetting and penetration, flexibility, and elasticity are favored by a long oil length. Short-oil alkyds have the best baking properties, greatest hardness and chemical resistance, highest gloss and chalking resistance, and best general durability. Intermediate properties for specific applications may be obtained with medium oil lengths. Solubility in polar solvents (e.g., ketones and esters) and compatibility with polar resins (e.g., cellulose nitrate and urea-formaldehyde) is greatest at the higher alkyd ratios (short oil length). With increasing oil length, the solubility and compatibility with polar solvents and resins decreases, and the alkyd resin becomes increasingly compatible with less polar resins (e.g., polystyrene and chlorinated rubber) and increasingly soluble in nonpolar solvents, first in aromatic hydrocarbons such as xylene and finally even in aliphatic hydrocarbons such as mineral spirits. An alkyd need not be greater in oil length than 65 gallons, since beyond this point the modified alkyd becomes freely compatible with drying oils, and oil can be added as required for particular applications. Long-oil alkyd resins for metal or wood priming paints often have some raw linseed mixed in to promote good wetting and penetration.

3.4.1.3. USES OF ALKYD RESINS.—Huge quantities of oil-modified glyceryl phthalate alkyds are used in interior and exterior enamels, architectural paints, wall paints, automotive finishes, appliance enamels, industrial finishes, and marine coatings. Long-oil, air-drying alkyds have very good elasticity and exterior durability, making them suitable for architectural trim paints (trim and trellis paints), garden furniture coatings, porch and deck enamels, and automotive refinishing enamels. In marine applications, alkyd finishes are often used above the water line for their good durability, while a phenolic varnish is used below the water line because of its better water resistance. Between the high and low water lines a vinyl-alkyd coating (sec. 4.3.1.2) gives good service. The long-oil alkyds also make excellent interior wall paints, either flat or gloss, that brush on easily and provide a long-lasting finish. Pentaerythritol type alkyds have fast air-drying characteristics despite a long oil length; although more expensive than glyceryl phthalate alkyds, they are more durable and make excellent white architectural trim paints and marine enamels.

Medium-oil and short-oil alkyds are often combined with other resins to make fast air-drying or baking-type colored finishes for toys, tools, and sundry items. Resin-and-oil modified alkyds find use in corrosion resistant primers for metal; for example, a phenolic-modified oil-

alkyd employing zinc yellow pigment is the basis for Fed. Spec. TT–P–666 zinc chromate primer [88] for use on aluminum and magnesium surfaces. Phenolic-modified alkyds are also used in interior finishes requiring improved alkali (soap) resistance.

Automotive finishes have progressed from the early alkyd-modified cellulose nitrate finishes to the highly durable present-day melamine-alkyd finishes in which a short-oil alkyd is combined with about 30 percent of melamine-formaldehyde resin to produce a fast-baking enamel with excellent hardness, gloss, color retention, and exterior durability. White baking enamels for kitchen cabinets, refrigerators, and other appliances are often based on short-oil, soybean alkyds combined with urea- or melamine-formaldehyde resin. For maximum whiteness and non-yellowing with heat or aging, non-oxidizing alkyds modified with non-drying oils, such as cocoanut or castor oil, are employed. Non-oxidizing alkyds in combination with melamine-formaldehyde resin make good heat-resistant finishes for lighting fixtures and stove enamels. The non-drying alkyds are also used as plasticizers in cellulose nitrate lacquers for furniture, automobiles, aircraft [56], machinery, and tools.

3.4.2. Resin-Modified Alkyds

3.4.2.1. STYRENATED-ALKYDS are being used effectively in very fast air-drying and baking finishes. The resin is prepared either by styrenating the oil with which the alkyd is to be reacted, or by direct styrenation of the oil-alkyd; in either case, the reaction is with styrene monomer. The polystyrene resin, besides being relatively low in cost, contributes its own good water and alkali resistance and good color retention properties to the styrenated-alkyd. However, styrenated-alkyds are not as durable on exterior exposure as the pure oil-modified alkyds, and the sensitiveness of polystyrene to oils and hydrocarbon solvents also manifests itself to some extent in the modified alkyd. The hydrocarbon sensitivity can be reduced, in the case of baking finishes, by adding an amino resin. Air-drying styrenated-alkyds usually contain metallic driers. With high pigment content and a solvent such as xylene, they will dry hard in about 10 minutes to a lusterless finish. For best flow in high gloss finishes, the styrenated-alkyd is dissolved in the slower-evaporating mineral spirits, and it dries hard in 3 to 6 hours. Styrenated-alkyds are used in fast-drying finishes for wood and metal furniture, household implements, toys, and interior applications requiring resistance to alkaline cleaners (e.g., washing machine coatings) but not subject to contact with oils and greases. Best resistance is obtained with baking finishes incorporating amino resins.

3.4.2.2. SILICONE-ALKYDS are copolymerized silicone and alkyd resins which combine the excellent heat resistance, water and chemical resistance, and electrical properties of the silicone resins with the good brushability, gloss, hardness, and durability of the alkyd resins (also see sec. 3.9.2.1). Silicone-alkyds are used in high-grade heat-resistant baked coatings for stoves, boilers, machinery, and electrical equipment. Because of their good water, alkali, and chemical resistance, they are also used to advantage in coatings for washing machines, industrial equipment, and kitchen equipment. Air-drying silicone-alkyds for industrial maintenance paints also have been developed.

3.4.2.3. OTHER RESINS WITH WHICH ALKYDS MAY BE CHEMICALLY COMBINED (in addition to the amino, phenolic, and other resins already mentioned) include epoxies, acrylics, and polyurethanes. The use of such resin combinations is just beginning to be exploited for coatings purposes. In general, the properties of the dual resin may be expected to be a combination of, or intermediate between, those of the individual constituents (see sec. 3.1.4.2).

3.4.3. Polyester Resins

Although in a general sense all alkyd resins are polyesters, since they are the product of an esterification reaction between a polyhydric alcohol and a polybasic acid, the term "polyester" is commonly used in a narrower sense to denote a linear-type alkyd possessing carbon-to-carbon double-bond unsaturation in the polymer chain. These unsaturated polyesters may be cross-linked by reaction with a monomer such as styrene or diallyl phthalate (often with a peroxide added also) to form an insoluble and infusible resin, without the formation of a by-product during the curing reaction. Although the chief use for the unsaturated polyester resins in the past has been in the low-pressure laminating field, the polyesters are now among the most promising of the newer resins finding application in the coatings field as attractive and durable finishes for concrete, masonry, wood, plaster, wallboard, and metal. On porous or rough surfaces (all the aforementioned except metal), reliance is placed primarily on mechanical adhesion ("bite" or penetration) rather than on specific adhesion (chemical attraction) to keep the coating in place. The good specific adhesion needed on smooth, nonporous surfaces of metal has been obtained by combining the polyester with an isocyanate polymer (see sec. 3.12.1.2) in addition to a styrene monomer hardening agent. Thorough surface preparation based on the principles given in chapter 6 and in accordance with the manufacturers instructions for filling, cleaning, sealing, and priming is very important for the successful

application of polyester coatings, and well-trained experienced personnel are required.

Since the uncured polyester resin can be made in a liquid form suitable for application without the addition of volatile solvents or thinners, a 100 percent solids coating system capable of high film build (10 to 20 mils per coat) is possible, and tile-like polyester coatings up to 40 mils in overall thickness are available for heavy duty applications. The hardening agent is mixed into the polyester resin just before it is applied. Curing proceeds throughout the coating by an exothermic, chemical crosslinking reaction at a rate dependent primarily on the coating temperature and on the type and concentration of hardening agent. A hard film is obtained in a few hours. The thickness of the coating affects the cure indirectly through its effect on the quantity of heat released and resultant temperature, and through its effect on the relative amount of hardener lost by volatilization at the surface, as determined by the ratio of surface area to coating volume. On the basis of these factors, a coating thickness of 6 mils is considered to be the minimum necessary to ensure adequate cure.

The tile-like polyester coatings are hard, nonporous, durable coatings capable of withstanding dilute alkalies and acids, organic solvents, hot water, and a high order of nuclear radiation (see sec. 4.6.8), as well as mechanical abuse, impact, and abrasion. The mechanical strength, toughness, and flexibility of polyester coatings can be greatly increased by incorporating glass fibers or by laminating glass fabric into the coating system. The glass fiber reinforcement is accomplished by chopping and blowing glass roving into a layer of wet coating by means of an electrical or air-driven chopper and then rolling in the fibers with another layer of coating material. Appearance is enhanced by depositing colored tracer threads along with the regular glass roving. Finally, a topcoat of polyester resin may be applied to provide a smooth finish. For the glass fabric reinforcement, the fabric is laid on the primed, dry surface, all wrinkles are worked out, and the fabric is saturated with the polyester applied by brush or roller to wet the fabric but not fill the weave. After the saturation coat is cured, it is sanded lightly and a heavy topcoat of polyester resin is applied to complete the coating system. The glass fabric reinforcement imparts maximum strength to the coating system.

USES for polyester resin coatings include hard lustrous clear finishes for furniture, water- and weather-resistant finishes for boats, durable and attractively colored coatings for the exteriors of concrete or masonry buildings, tough impact- and abrasion-resistant coatings for corridor walls and floors of schools and hospitals, wear- and wash-resistant sanitary coatings for cafeteria and hospital kitchens and for dust-free rooms, decontaminable and radiation-resistant coatings for walls and floors of atomic facilities, hot water- and radiation-resistant coatings for canal walls and floors of nuclear reactors, tough wear-resistant coatings for stairways, bowling alleys, and gymnasium floors, coatings for swimming pools, and industrial coatings for metal structures and equipment.

3.5. Amino Resins

The amino resins (or aminoplasts, as they are sometimes called) that are of chief importance are the urea- and the melamine-formaldehyde compounds. The urea resins have been available since 1930 and the melamine resins since 1940.

3.5.1. Properties

The amino resins are thermosetting materials that readily form hard, brittle, colorless, chemically resistant films on baking. Because of their brittleness and poor adhesion when used alone, they require proper plasticization for use in coatings. This is usually accomplished by combining them with short- or medium-oil alkyds. The amino-alkyd blend provides an excellent combination of coating properties in which the adhesion, toughness, gloss, and durability of the alkyd are complemented by the baking speed, hardness, color retention, and chemical resistance of the amino component. The amino resin is used as the minor component and usually constitutes from 15 to 35 percent of the resin solids, although it may be as low as 5 to 10 percent in some automobile finishes and as high as 50 percent in some low-bake furniture finishes.

3.5.2. Formation

The formation of amino resins proceeds in three stages. In the first stage methylol amine monomers are formed by reaction of urea or melamine with formaldehyde under mildly alkaline conditions. In the second or intermediate stage, these monomers condense to form linear water-soluble polymers which are partially etherified with alcohols (usually butanol) as the polymerization proceeds, to confer organic-solvent solubility. In the third and final stage, the resin is converted by heat to a cross-linked, thermoset, infusible, insoluble resin.

3.5.3. Uses

The excellent combination of coating properties (see above) possessed by the urea and melamine alkyd resins has led to their wide use,

singly or together, in high-grade, fast-baking, durable, mar-resistant, chemically resistant finishes for automobiles, refrigerators, washing machines, stoves, electrical appliances, hospital equipment, counter tops, furniture, and other industrial and household applications.

3.5.4. Comparison of Urea and Melamine Resins

Although there are many similarities in the preparation, properties, and uses of urea and melamine resins, there are also important differences which influence the selection of one or the other (or a combination of both) for a particular application. The urea-formaldehyde resins are lower in cost, have better adhesion properties, are more amenable to the repair of coating defects, and yield (in combination with an alkyd) excellent white enamels that are as good or better in color retention than the melamine-alkyds at moderate baking temperatures (below 300 °F [149 °C]) and in indoor service at moderate temperatures. The melamine-alkyds, although considerably more expensive, are much faster-curing, undergo less shrinkage during cure, have better color and gloss retention on overbaking and in elevated temperature applications, are more chemical-resistant, have superior hardness and mar resistance, and possess better exterior durability. Melamine resins, though capable of very fast cures at high temperatures without color impairment, may also be cured quite rapidly at lower temperatures and therefore are very adaptable to infrared baking schedules. Because of their greater functionality and faster cure, the melamine resins are generally used in lower proportions than the urea resins. In general, then, it may be stated that the urea resins yield coatings having an excellent combination of color retention, chemical resistance, and durability properties at relatively low cost. The melamines, though considerably higher in cost, extend the range of desirable properties still further and are used to particular advantage in applications requiring very fast cure, prolonged resistance to elevated temperatures, superior alkali resistance, maximum hardness, and outdoor durability. As a single example, a urea-alkyd produces a gleaming white refrigerator enamel of excellent durability at relatively low cost; on the other hand, for a heat-resistant stove enamel or an alkali-resistant washing machine finish, the melamine-alkyd would be the preferred coating material.

3.6. Vinyl Resins

In a broad structural sense, all resins derived from the vinyl radical ($CH_2 = CH-$) may be classified as vinyl resins. However, such a broad classification would include many types of resins that are better known by more familiar individual designations such as polyethylene, polystyrene, acrylic, and others. The term "vinyl resin" is applied here in the narrower sense commonly employed in the plastics and coatings field. Thus, vinyl resins include chiefly the polymers and copolymers of vinyl acetate, vinyl chloride, and vinylidene chloride, and the polyvinyl acetals and polyvinyl alcohol that are derived from polyvinyl acetate.

Vinyl resins are thermoplastic, addition polymers that may be prepared by solution, suspension, emulsion, or bulk polymerization methods (see sec. 3.1.3). Structurally, they may be thought of as substituted ethylenes in which one or two hydrogen atoms have been replaced by a chlorine atom, an acetate radical, an hydroxide group, or an acetal ring structure. In properties, they range from soft, tacky, widely soluble polymers to tough, horny, difficultly soluble ones, depending on their composition, molecular weight, and molecular structure. Since first achieving commercial importance in the early 1930's, their use has grown steadily, and vinyl resins constitute one of the most versatile and widely used classes of resins in the coatings field.

3.6.1. Polyvinyl Acetate

Polyvinyl acetate is produced either as a granular resin or as a dispersion in water (latex). The latex was discussed in section 2.3.5 on Latex Paints. The granular resin is usually prepared by solution polymerization; the vinyl acetate monomer is heated, in a solvent such as benzene or toluene, in the presence of a peroxide catalyst. The resulting polymer is a colorless, odorless, tasteless, nontoxic resin that is widely soluble in most of the common organic solvents such as the lower ketones, esters, methanol, higher alcohols containing some water, aldehydes, aliphatic acids, aromatic and chlorinated hydrocarbons, and nitrohydrocarbons. Polyvinyl acetate is less soluble or insoluble in the higher homologs. It is insoluble in aliphatic hydrocarbons, in animal and vegetable fats and oils, and in water—but it swells and loses strength upon prolonged immersion in water. Polyvinyl acetate is compatible with many of the common ester-type plasticizers such as dibutyl phthalate (but not dioctyl phthalate), phosphates, abietates, and glycolates. Other materials with which it is partially or completely compatible include cellulose nitrate, cellulose ethers, chlorinated rubber, some phenolic resins, and a few acrylic resins and natural resins.

Polyvinyl acetate is light-stable, transparent to solar ultraviolet and visible light, abrasion-

resistant, flexible, and very resistant to outdoor aging. However, it softens at temperatures above 150 °F (66 °C), swells and weakens upon prolonged immersion in water, is hydrolyzed by strong acids or alkalis, and dissolved by many organic solvents. Its many desirable properties, coupled with good ahesion and ease of formulation and application, have led to its extensive use in the coatings field, as well as in the related field of adhesives. The latex form has found wide acceptance in primer-sealers, interior wall finishes, and exterior masonry paints. In emulsion or solution form, polyvinyl acetate is used as a water- and grease-resistant coating on paper, fabrics, and leather. Such coatings can be easily heat-sealed or solvent-sealed if desired, and they are widely used in food packaging. Lacquers based on polyvinyl acetate solutions find use as decorative and protective coatings for paper, wood, and metal. Suitably formulated PVA coatings have shown very good adhesion, durability, and corrosion resistance when applied to metals.

In addition to its compatibility with other resins as noted above, vinyl acetate can be copolymerized with various vinyl derivatives such as vinyl chloride, styrene, and acrylics to yield other materials with very desirable properties.

3.6.2. Polyvinyl Chloride

3.6.2.1. GENERAL PROPERTIES.—Polyvinyl chloride is a tough, horny, transparent, thermoplastic resin having high inherent strength and excellent chemical resistance. Its properties stem in part from its crystalline nature. It is highly resistant to strong acids and alkalis, water, alcohols, aliphatic hydrocarbons, fats, and oils—but it is swelled by aromatic hydrocarbons. It is soluble in only a few special types of solvent, chiefly unsaturated ketones (e.g., mesityl oxide and isophorone) and alicyclic compounds (e.g., cyclohexanone and tetrahydrofuran). It is soluble also in nitrobenzene and in dimethyl formamide. Because of this very limited solubility in organic solvents, polyvinyl chloride is not widely used in solvent-type coatings; however, in the form of a plastisol or organosol (discussed below) that is readily applied by dipping or knife-coating methods, it finds extensive use in severe service applications.

Polyvinyl chloride is made chiefly by suspension or emulsion polymerization. The resin is available as a general-purpose granular white powder, as a fine-particle paste dispersion for use in plastisols and organosols, and as a water-base latex. In each case, the key to its effective use is suitable plasticization and stabilization. The unmodified resin, though tough and chemically resistant, is not flexible enough for coatings use unless plasticized, and it is degraded by heat and by ultraviolet light unless properly stabilized. The degradation reaction produces HCl which catalyzes further degradation unless the acid is removed as it forms. Fortunately, a large number of very effective heat and light stabilizers for polyvinyl chloride have been developed. These function as HCl acceptors or neutralizers, ultraviolet absorbers, and antioxidants to impart excellent stability to the resin.

The general-purpose polyvinyl chloride resin finds wide use in high-grade electrical insulating coatings for wire and cable; it combines excellent dielectric strength with flexibility and toughness, resistance to moisture and chemicals, and fire resistance. The plasticized resin may also be calendered onto paper or fabric to provide tough, water-proof and grease-proof coatings; however, polyvinyl chloride surface coatings are most conveniently applied in the form of plastisols or organosals (see below). The use of plasticized polyvinyl chloride film and sheeting for shower curtains, inflatables, upholstery, etc., is so extensive as to merit mention even in a discussion of coatings.

3.6.2.2. PLASTISOLS and ORGANOSOLS.—*Plastisols* are dispersions of finely divided polyvinyl chloride resins (dispersion resins) in suitable liquid plasticizers. The dispersion resins are powders of very fine particle size (0.05 to 1.0 micron in diameter) made by emulsion polymerization. Among suitable plasticizers are compounds such as dioctyl phthalate, tricresyl phosphate, other alkyl and aryl phthalates and phosphates, adipates, sebacates, and azelates. Plastisols may be applied in a thick coat, by dipping or knife-coating, to paper, cloth, wood, and metal. The deposited coating is then fused by flash-heating at 300-350 °F (149–177 °C) to yield a tough, durable, chemically resistant film. *Organosols* are similar to plastisols, except that they contain some organic solvent to facilitate application of the coating for purposes requiring a lower viscosity. Upon evaporation of the organic solvent, the deposited coating is fused by flash-heating just as in the case of the plastisol. Organosols and plastisols are used for coatings on lawn furniture, office equipment, industrial equipment, and home appliances. They give excellent service in such severe applications as coatings for plating baths, chemical tanks, and dish-washer racks.

Aside from the external plasticization of polyvinyl chloride as in plastisols and organosols, the resin can be modified for use in solvent-type coatings by copolymerization with vinyl acetate to provide permanent internal plasticization, as described in the following section.

3.6.3. Polyvinyl Chloride-Acetate

Polyvinyl chloride-acetate is made by the copolymerization of vinyl chloride and vinyl acetate, the chloride constituting from 85 to 97

percent of the copolymer. Solution or suspension polymerization methods are usually employed. The vinyl chloride-acetate copolymers retain much of the toughness and chemical resistance of polyvinyl chloride while partaking of the greater flexibility and solubility of polyvinyl acetate. The copolymers are easily formulated into solution-type coating materials for either air-drying or baking applications. A few types are made as dispersion resins for use in plastisols and organosols (see previous section). Like the parent polyvinyl chloride, the copolymers must be stabilized against the deteriorating effects of heat and ultraviolet light. Plasticizers, pigments, and fillers are incorporated as required for particular coatings applications. Polyvinyl chloride-acetate copolymers are soluble in ketones, esters, ethers, and chlorinated hydrocarbons. Aromatic hydrocarbons such as toluene and xylene are well-tolerated diluents and are nearly always part of the composite solvent formulation. In addition to their availability in a range of chloride-to-acetate ratios and a variety of molecular weights, vinyl chloride-acetate resins may be copolymerized with a small proportion (about 1%) of maleic resin to impart improved adhesion of air-drying coatings to smooth metal surfaces. Vinyl copolymers without the maleic resin must be baked to develop good ahesion to smooth metals, but they adhere well to porous surfaces of paper, fabric, leather, and concrete.

Most unmodified vinyl chloride-acetate copolymers are poorly compatible with other resins. However, when modified by incorporating hydroxyl groups, the copolymer becomes compatible with various alkyd, phenolic, amino, and other resins. Compatibility with nitrocellulose can be obtained with copolymers of high acetate content.

Vinyl chloride-acetate copolymer coatings are odorless, tasteless, and nontoxic (unless rendered otherwise by modifying ingredients). The coatings are tough and flexible, resistant to water and chemicals, non-flammable, abrasion-resistant, and weather-resistant.

USES. Polyvinyl chloride-acetate resins find wide and important use in the coatings field. Their lack of taste, odor, or toxicity makes them well suited for coating food and beverage containers. Their flexibility and adhesion permit their use on flat sheet metal that must withstand subsequent deep drawing or stamping operations. Their chemical resistance makes them suitable as coatings for the insides of drums and tanks and pipes that must carry corrosive chemicals. Their alkali resistance permits their use over concrete, plaster, and alkaline wallboards without special precautions. Wrinkle and textured coatings based on these resins can be applied to paper, cloth, wood, and metal to produce durable and attractive finishes; textured finishes for high-quality radio and amplifier cabinets, which impart a furniture-like appearance to the metal cabinets, have become popular. Other uses include coatings for garden furniture, metal signs, hospital and kitchen furniture that must withstand wear and frequent washing, refrigerator parts, collapsible tube coatings, perspiration-resistant articles, and specially-formulated strippable coatings. The combination of toughness and resistance to weather, water, and chemicals possessed by the vinyl-chloride acetate copolymers makes them valuable coatings for use in durable, corrosion-resistant coating systems for severe industrial and marine applications (see sec. 4.3.1.2); for example, the coating system selected for protecting the locks of the St. Lawrence Seaway is based on vinyl copolymer resins.

3.6.4. Polyvinyl Alcohol

Since vinyl alcohol does not exist in monomeric form, polyvinyl alcohol cannot be prepared by direct polymerization. Instead, it is obtained by the hydrolysis of polyvinyl acetate in an essentially water-free alcohol medium (usually methanol) in the presence of small amounts of acid or alkaline catalysts. The properties of the final resin depend largely on the degree of hydrolysis and on the molecular weight. With increasing hydroxyl content (increasing polar character) the polymer becomes less hydrophobic and more hydrophilic. When about 65 percent of the original acetate groups have been hydrolyzed (replaced by hydroxyl groups), the product loses its solubility in organic solvents and becomes soluble in cold water but precipitates on heating. With further hydrolysis, when about 80 to 90 percent of the acetate groups have been replaced with hydroxyl groups, the product is soluble in both cold and hot water. When the hydrolysis is virtually complete (95 percent or more of the acetate groups replaced), the polyvinyl alcohol will no longer dissolve in cold water; but if dissolved in hot water, it will remain in solution on cooling.

Coatings deposited from solutions of polyvinyl alcohol in water are tough and flexible and highly resistant to water-insoluble organic solvents such as aromatic, aliphatic, and chlorinated hydrocarbons, and vegetable and animal fats and oils. Polyvinyl alcohol coatings are highly impermeable to most gases, have high tensile strength, and are odorless and tasteless.

Polyvinyl alcohol resins can be applied to paper, fabrics, and leather to provide a highly grease- and gas-resistant coating. In combination with a water-resistant film or coating, an effective barrier against water, gases, greases, and most organic solvents can be obtained. Polyvinyl alcohol is a versatile emulsifying agent and finds use as an emulsifier, thickener,

and stabilizer in emulsion polymerizations and latex paints.

The flexibility of polyvinyl alcohol films and coatings can be increased by incorporating water-soluble plasticizers such as glycerol, the lower glycols, and various amines. A number of processes have been patented for insolubilizing polyvinyl alcohol coatings through metal complexing or through reaction with other resins such as phenolics, melamines, and diisocyanates. A weather-resistant polyvinyl alcohol water-base coating has been described [57] which is formulated so as to form insoluble acetals (without baking) that resist solution in water while retaining good resistance against penetration by gases and by organic solvents and vapors.

3.6.5. Polyvinyl Acetals

Polyvinyl acetals are the products of the condensation reaction between polyvinyl alcohol and aldehydes. The aldehydes of commercial importance for this use are formaldehyde, acetaldehyde, and butyraldehyde. The reaction can be controlled to yield acetals having various ratios of acetate, hydroxyl, and acetal groups. In general, solubility decreases while viscosity and strength increase with increasing degree of acetalization. The resins are usually supplied as powders which may be compounded with plasticizers and other resins to produce tough, elastic, water-insoluble coatings.

3.6.5.1. POLYVINYL FORMAL is the toughest of the vinyl resins. It has a tensile strength of about 20,000 psi, a softening temperature of about 375 °F (191 °C), and a water absorption of about 1 percent. It is unaffected by aliphatic hydrocarbons, gasoline, oils, fats, waxes, and alkalies, but it is soluble in chlorinated hydrocarbons, dioxane, phenol, and aliphatic and cyclic ethers. It has excellent abrasion resistance and electrical properties, and a chief use has been in combination with phenolic resins as a tough, flexible, electrical insulating coating for wire. It has also been used as the inner gasoline-resistant liner of self-sealing "bulletproof" gasoline tanks, as an abrasion-resistant coating for wooden propellers of aircraft, for can linings, and in metal primers.

3.6.5.2. POLYVINYL ACETAL is a slightly yellowish, odorless and tasteless resin that is widely soluble in ketones, esters, alcohols, and chlorinated hydrocarbons, but insoluble in aromatic and aliphatic hydrocarbons, oils, and water. Its tensile strength (about 8000 psi) and its softening temperature (about 320 °F) [160 °C] are considerably below that of polyvinyl formal, and it has a somewhat higher water absorption (about 2 percent). Although used chiefly in adhesives, it finds limited use in coatings for fabrics and, in combination with cellulose nitrate, in interior coatings for household articles.

3.6.5.3. POLYVINYL BUTYRAL is best known for its wide use as the clear, tough interlayer in safety glass. However, it also performs excellently in the coatings field and has proved particularly useful as a base for wash primers (see sec. 6.3.2.5) and metal conditioners. As made commercially, polyvinyl butyral resins contain a considerable percentage of hydroxyl groups (about 7 percent) which impart a hydrophilic character to the resin and contribute to its excellent specific adhesion to nonporous surfaces such as glass, metal, and phenolic plastics. Polyvinyl butyral coatings also have very good adhesion to porous surfaces such as wood, paper, and fabrics. Baking is not required to develop good adhesion.

Polyvinyl butyral is soluble in non-anhydrous alcohols, glycol ethers, and some esters and ketones. Water is an effective latent solvent; in fact, 3 to 8 percent must be present to achieve good solvent properties. Mixed thinners containing about 40 percent alcohol with esters, ketones, aromatic hydrocarbons, and a small amount of water are excellent solvents for use in coatings formulations based on polyvinyl butyral. Although flexible enough for many coatings applications without added plasticizer, polyvinyl butyral resins may be compounded with various chemical plasticizers, such as trioctyl phosphate, triethylene glycol di (2-ethylbutyrate), and dibutyl sebacate, to increase their flexibility and to decrease their viscosity in hot melt applications (e.g., in high-speed book-binding).

Polyvinyl butyral is compatible with phenol-, urea-, and melamine-formaldehyde resins and can be cured or cross-linked by heating with these resins. Air-dry cure and crosslinking can be accomplished by the addition of glyoxal. Crosslinked polyvinyl butyral coatings are tough, heat-resistant, and solvent-resistant; they have been used for gasoline tank linings, can coatings, laboratory equipment, and as waterproof cloth coatings replacing rubberized fabrics.

An effective knot sealer (WP–578) developed by the Western Pine Association is based on a combination of polyvinyl butyral with a phenolic resin in ethanol (95%) solution [149]. The sealer may also be applied over asphaltic materials to prevent bleeding into enamel topcoats. Polyvinyl butyral may be used as a heat-sealable coating for foil and other packaging materials. Durable wood finishes can be made from combinations of polyvinyl butyral with shellac or with phenolic resins. The most important application of polyvinyl butyral in the coatings field, however, has been as the base for corrosion-inhibiting metal primers (wash

primers) utilizing chromate pigments for corrosion inhibition, and phosphorc acid to achieve metal conditioning and cross-linking of the coating [30]. Such wash primers have excellent adhesion to metal substrates and to virtually any type of topcoat lacquer or paint (except a few types of nitrocellulose and vinyl lacquers). Excellent all-vinyl-base coating systems for severe marine applications employ a polyvinyl butyral wash primer as the first coat applied to the metal (see sec. 4.3.1.2).

3.6.6. Polyvinylidene Chloride and its Copolymers

3.6.6.1. POLYVINYLIDENE CHLORIDE is a tough, nonflammable, crystalline resin characterized by extremely low water vapor permeability and absorption, and outstanding resistance to oils, greases, acids, alkalis (except strong ammonium hydroxide), and most organic solvents and reagents. It is soluble only in cyclic ethers and cyclic ketones, but is attacked and weakened by halogens and strong organic amines. Because of its extremely limited solubility and compatibility with other materials, polyvinylidene chloride itself has not in the past been used in the coatings field; however, a polyvinylidene chloride latex for coatings applications requiring exceptional water and chemical resistance is now available. When polyvinylidene chloride is internally plasticized by copolymerization with vinyl chloride or acrylonitrile, very useful coatings resins are obtained.

3.6.6.2. POLYVINYLIDENE CHLORIDE COPOLYMERS (general). The copolymers (commonly known as saran resins in the trade) have a less crystalline and less closely packed structure than the polyvinylidene chloride homopolymer because of the irregularities introduced into the polymer chains by the random presence of the copolymerized vinyl chloride or acrylonitrile groups. The reduced crystallinity of the copolymers increases their solubility and compatibility and permits their use in solution-type coatings and in plasticized latexes. It is of general interest to note that the irregular arrangement of vinyl and vinylidene groups in the copolymer chains produces a fairly soluble and compatible resin even though both polyvinyl chloride and polyvinylidene chloride are themselves only narrowly soluble and compatible materials (cf. discussion of crystallinity in sec. 3.1.1. A range of properties is achieved by varying the copolymer ratio and system. In general, commercial polyvinylidene chloride-acrylonitrile copolymers for coatings contain a low proportion of acrylonitrile, whereas polyvinylidene chloride-vinyl chloride copolymers may vary in composition from low to high ratios of vinyl chloride. The copolymer latexes, although convenient to use, are not quite as water-impermeable or chemically resistant as the solution-type coatings, largely because of the water-sensitive emulsifiers, stabilizers and other additives that remain in the cured latex film.

3.6.6.3. VINYLIDENE CHLORIDE-VINYL CHLORIDE COPOLYMERS possess their maximum solubility, compatibility, and flexibility when they contain approximately equal proportions of vinyl and vinylidene groups. Tensile strength and softening temperature are higher when either monomeric group predominates. Color stability is better with higher vinyl chloride content; as with straight vinyl chloride resins, the copolymer resins require heat and ultraviolet stabilizers for best results. A typical copolymer of medium or somewhat higher vinyl chloride content is soluble in ketones, cyclic ethers, and amides; it has a high tolerance for aromatic hydrocarbon diluents and exhibits good compatibility with the common vinyl plasticizers, as well as with many alkyds and a few other resins; it has excellent resistance to water, chemicals, and many organic solvents, indicating a potential usefulness for maintenance coatings and marine finishes. A copolymer of high vinylidene chloride content is available which is soluble in aromatic hydrocarbons and in mixtures of aromatic hydrocarbons with ketones, and which is compatible with many common vinyl plasticizers and a few other resins. Another type, a latex, does not form films alone but is compatible with a number of water dispersable materials and oleoresinous and alkyd resins to which it contributes toughness and water resistance. In general, vinylidene chloride-vinyl chloride copolymers are used in applications requiring exceptional resistance to water, acids, alkalis, and many solvents, and a high degree of impermeability to water vapor and gases.

3.6.6.4. VINYLIDENE CHLORIDE-ACRYLONITRILE COPOLYMERS of high vinylidene chloride content are available as solution or emulsion types. The resin is soluble in methyl ethyl ketone and in various cyclic and unsaturated ketones and will tolerate limited amounts of diluents. It has sufficient flexibility to permit its use without plasticization in coatings where maximum chemical and solvent resistance are needed. Where greater flexibility is required, the resin may be plasticized with various phthalates, phosphates, glycolates, or sebacates. Although vinylidene chloride-acrylonitrile copolymers have a limited compatibility with a few other resins, they are usually used alone because of the better chemical resistance of the unmodified resin. Coatings based on these resins find use in the packaging industry where they are applied to paper, fabrics, and metal foil to provide heat-sealable, chemical-resistant,

grease-proof, and water-proof coatings. Other uses include cap linings, coatings for the interior of gasoline storage tanks, drum coatings, chemical-resistant maintenance paints, and strippable cobweb coatings (see sec. 2.2.7) for protecting instruments and machinery against moisture and corrosion during shipment and storage. A water- and fuel-resistant lacquer [150] based on a vinylidene chloride-acryonitrile copolymer is covered by Mil. Spec. MIL–L–18389.

3.6.7. Polyvinyl Ethers

Among the polyvinyl ethers, only the alkyl types are of sufficient importance to warrant brief mention here. These include the methyl, ethyl, isobutyl, and n-butyl polyvinyl ethers, and a copolymer of vinyl methyl ether with maleic anhydride. The polyvinyl alkyl ethers are linear, thermoplastic, tacky polymers that are widely soluble in organic solvents and widely compatible with other resins. The vinyl ether/maleic acid copolymer is soluble in water as well as in organic solvents; the vinyl methyl ether homopolymer is soluble in cold but not in hot water.

The chief application for the polyvinyl alkyl ethers has been in pressure-sensitive tapes, polyvinyl ethyl ether being particularly useful in this respect in combination with phenolic varnish resins. In the coatings field, the polyvinyl ethers are finding some use as plasticizing agents in chlorinated rubber paints and cellulose nitrate lacquers, and as binding agents in paints and impregnating solutions. Polyvinyl methyl ether can be used as a nonionic heat-sensitizing or softening agent in latex paints to improve film coalescence and adhesion.

3.7. Acrylic Resins

3.7.1. Properties

The acrylic resins of chief importance in coatings are the polymers and copolymers of acrylic and methacrylic acid esters. They are thermoplastic, addition-type polymers that range in physical properties from soft, sticky semiliquids to hard, machinable solids, depending on their composition and molecular weight. The acrylates are softer, more extensible, and more soluble than the corresponding methacrylates. Softness, extensibility, and solubility are also greater with increasing number of carbon atoms in the alcohol side-chain. With the wide range of properties obtainable by varying the alcohol side-chain, and with the additional opportunities for variation afforded by copolymerization of various acrylates and methacrylates, it is possible to produce resins having almost any desired degree of flexibility without the use of plasticizers. The latter is an important advantage, since the unmodified acrylic ester polymers possess a clarity and a resistance to discoloration by aging, heat, and ultraviolet light that is unsurpassed by any other resin. Other desirable properties of acrylic resins which have led to their wide use in coatings and plastics since their introduction around 1931 are: wide solubility in common organic solvents, permitting ease and economy of formulation; excellent resistance to acids (except concentrated oxidizing types), alkalis, water, alcohols, aliphatic hydrocarbons, oils, and greases; low acid number and low reactivity with pigments; and good adhesion to a variety of surfaces. Although acrylic coatings air-dry satisfactorily, optimum film properties are developed by baking.

While the degree of solubility (and the solution viscosity) of the acrylic resins depends on their composition and molecular weight, as noted above, they are, in general, soluble in aromatic and chlorinated hydrocarbons, esters, and ketones. A few special types are available which are soluble in alcohol and in mineral spirits, but in most instances the alcohols and aliphatic hydrocarbons are non-solvents. The acrylic resins have only limited compatibility with each other and with other classes of resins; however, their monomers are readily copolymerized with other addition-type monomers. Some types of acrylic resin are compatible with nitrocellulose, ethyl cellulose, and some of the vinyl resins. They are not compatible with drying oils, oleoresinous varnishes, or oil-modified alkyds. Where plasticization is desired for special purposes, the acrylic ester resins may be combined and are compatible with some of the common chemical plasticizers such as dibutyl phthalate, tricresyl phosphate, and dibutyl sebacate.

The acrylic resins are available in emulsion form as well as solution-type resins. In emulsion form they have found wide acceptance in latex paints and primer-sealers for both interior and exterior applications. The characteristic heat and light stability and chemical resistance of the solution-type acrylic resins are also found in the latex form. A discussion of acrylic latex paints is given in section 2.3.5.6.

3.7.2. Uses

Because of their versatility and excellent combination of properties, the acrylic resins find many uses in the coatings field. In addition to their large-scale use in latex paints, they are used in protective and decorative lacquers for paper, fabrics, leather, plastics, wood, and metal. Clear acrylic coatings are used to pro-

tect paintings and other art objects, to preserve important documents, to prevent the tarnishing of silverware, to protect bright metal against outdoor corrosion, and as electrically insulating coatings. White baking enamels having excellent resistance to chemicals and chemical fumes can be made with acrylic resins. Acrylic vehicles are also used in luminescent paints. Recently a high-gloss, hard, weather-resistant finish based on acrylic resins has been developed and adopted for use on automobiles. Thermosetting types of acrylic resins have been developed [124] which cross-link upon heating to form hard, insoluble and infusible coatings that are suitable for appliance finishes that must withstand severe service, such as those on washing machines, stoves, and dishwashers. A water-thinnable vehicle for industrial baking finishes utilizing a new thermosetting acrylic emulsion polymer [123] is reported to have a hardness, impact resistance, adhesion, and durability superior to that of premium melamine-alkyd baking finishes while being equal to melamine-alkyds in gloss and stain resistance. Since the acrylic ester monomers are readily copolymerized with other vinyl monomers, an important use for the acrylics has been to provide internal plasticization for polymers of vinyl chloride, vinylidene chloride, vinyl acetate, acrylonitrile, styrene, and others. An acrylic-nitrocellulose gloss lacquer [138] is covered by Mil. Spec. MIL–L–19537.

3.8. Polystyrene and Its Copolymers

The styrene monomer is readily polymerized by bulk, solution, suspension, or emulsion methods (see sec. 3.1.3) in the presence of a peroxide catalyst and mild heat. Very high molecular weights (greater than 1,000,000) can be obtained; however, most commercial polystyrenes are considerably lower in molecular weight (about 125,000 for molding grades and about 35,000 for grades used in surface coatings). Styrene is also readily copolymerized with a variety of other materials, including drying oils, butadiene, phenolics, vinyls, acrylics, maleic esters, and various unsaturated dicarboxylic acids. Substituted styrenes, such as α-methyl styrene, vinyl toluene, etc., also polymerize readily. The polystyrene family of resins is therefore a large one, and a variety of properties is obtainable depending on the composition and the degree of polymerization.

3.8.1. Polystyrene Homopolymer

Polystyrene itself is a hard, glasslike, colorless, transparent, thermoplastic resin. It is soluble in aromatic and chlorinated hydrocarbons and in some esters and ketones. It is highly resistant to acids (except strong oxidizing types), alkalis, alcohols, and vegetable fats and oils. Although somewhat permeable to water vapor, its water sorption is extremely low, and it is highly resistant to and dimensionally stable in water. It has excellent electrical properties. The chief use for unmodified polystyrene is in the plastics molding field. Polystyrene is not widely used alone as a coating because of its brittleness, although it is readily applied from solution for coatings applications in which flexibility is not a requirement (e.g., as a grease-, stain-, and perspiration-resistant protective coating on hard book covers, stiff leather and fabrics, labels on rigid substrates, and as an electrically insulating coating). The copolymers of polystyrene with butadiene and with drying oils, however, find extensive use in coatings.

3.8.2. Styrene-Butadiene Copolymers

Styrene-butadiene copolymers range from hard, brittle solids to soft, rubbery materials, depending on the ratio of styrene to butadiene. High butadiene types constitute the widely used GR–S (now termed SBR) synthetic rubbers. The high styrene types, containing about 60–80 percent styrene, are used in coatings. Being non-polar hydrocarbon resins, they are insoluble in water, alcohols, and other strongly polar solvents, but they are soluble in aromatic and chlorinated hydrocarbons and in mixtures of aromatic hydrocarbons with aliphatic hydrocarbons and ketones. They are resistant to acids, alkalis, mineral oils, and animal and vegetable fats and oils. Although thermoplastic and possessing a low softening temperature (about 125 °F [52 °C] for the solution types), they are heat stable at temperatures as high as 300 °F (149 °C). Both flexibility and adhesion are greater than that of the polystyrene homopolymer.

The chief application for styrene-butadiene copolymers in the coatings field has been in the water-base latex form. The first latex paints to be developed were of the styrene-butadiene type, and these are still among the leading materials in the huge gallonage of interior latex paints now marketed (see sec. 2.3.5). To a lesser, but still considerable, extent the styrene-butadiene copolymers also find use in exterior latex paints. They are also used as greaseproof, chemical-resistant, heat-sealable coatings for paper and fabrics.

Solution-type styrene-butadiene resins also find wide use in coatings. Their combination of excellent water and chemical resistance, toughness and abrasion resistance, good adhesion, and fast drying properties have led to their use in traffic paints, masonry paints, con-

crete floor enamels, swimming pool paints, metal primers, industrial maintenance paints, and general-purpose exterior coatings.

3.8.3. Styrenated Oils and Alkyds

Although polystyrene cannot be physically mixed with drying oils because of incompatability, the styrene monomer is readily copolymerized with drying oils having conjugated unsaturation (e.g., tung oil and dehydrated castor oil). Non-conjugated drying oils, such as linseed or soybean oil, may be successfully styrenated if they are first mixed with oils of the conjugated type. The styrenated oils yield fast-drying, hard, moisture-resistant films that have fair durability.

Improved durability is obtained by copolymerizing styrene with alkyds. The alkyd may be styrenated directly or a styrenated oil may be used (see sec. 3.4.2.1). Styrenated alkyds, while exhibiting some of the sensitiveness of polystyrene to aromatic solvents, have better acid and alkali resistance than ordinary oil-alkyds. Although not as durable on exterior exposure as the pure oil-modified alkyds, the styrenated alkyds find considerable use in low cost household and industrial finishes where fast drying is required along with good protective properties. Long-oil styrenated alkyds also find use as plasticizers for vinyl, amino, and cellulose nitrate lacquers.

3.8.4. Other Styrene Derivatives

3.8.4.1. COPOLYMERS of styrene with phenolic resins are used in coatings for porous surfaces and in household maintenance finishes. Styrene-isoprene copolymers with properties somewhat similar to styrene-butadiene copolymers have been produced. Styrene-maleic anhydride copolymers find use as emulsifying and stabilizing agents in latex formulations. The polymers of styrene and acrylonitrile are resistant to aromatic hydrocarbons but soluble in ketones; they have not been used much as coatings.
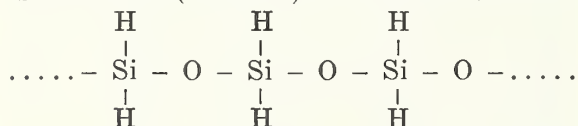
3.8.4.2. α-METHYL STYRENE is useful as a moderating comonomer in the mass copolymerization of styrene with the more reactive drying oils; by slowing the polymerization rate, it permits better control of the process.

3.8.4.3. VINYL TOLUENE POLYMERS and copolymers are a promising and increasingly useful class of resins for coatings. The name "vinyl toluene" refers to the ortho-, meta-, and para-substituted methyl styrenes, as distinguished from α-methyl styrene. The vinyl toluene polymers are more flexible and more widely soluble and compatible than their polystyrene counterparts. Like styrene, vinyl toluene can be copolymerized with drying oils, oil-modified alkyds, and various addition-type monomers, yielding a very versatile and useful class of resins having a wide range of desirable properties. The reaction of vinyl toluene with drying oils in the presence of divinyl benzene as a cross-linking agent produces alkyd-like resins that are more stable and alkali-resistant than ordinary alkyds because they have a carbon-to-carbon instead of an ester-type cross-linkage. Among the more recent developments in vinyl toluene resins are copolymers with butadiene and other dienes; these are soluble in organic solvents and constitute a promising class of coatings resins.

3.9. Silicone Resins

3.9.1. Pure Silicone Resins

Silicone polymers are organosilicon compounds of high molecular weight, consisting of an inorganic backbone chain of silica (alternate Si and O atoms) with organic radicals attached to this main chain through C–Si linkages. The basic silicone (siloxane) structure is:

$$\cdots\cdots - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{Si}}}} - O - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{Si}}}} - O - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{Si}}}} - O - \cdots\cdots$$

Replacement of the hydrogen atoms with various alkyl and aryl groups yields a very large and very useful class of polymers (organopolysiloxanes) that are characterized by outstanding heat resistance, excellent water resistance and water repellency, excellent electrical properties, and very good weatherability. The silicones have been available since about 1944. Both linear and crosslinked types are produced.

The low molecular weight linear polymers are heat- and oxidation-resistant fluids. The high molecular weight linear polymers are elastomers. The crosslinked types, in a range of molecular weights, are the silicone resins used as coatings. Crosslinking is generally accomplished by introducing trifunctional silicon atoms (having a third oxygen atom attached in place of one of the organic substituent groups) at intervals along the siloxane chains to form oxygen bridges between trifunctional atoms on different chains. Ways have been developed also for accomplishing the crosslinking through polyfunctional organic side-groups.

Although the solubility, compatibility, and chemical resistance of the silicone resins vary with the nature of the side groups and the molecular weight, they are generally soluble in chlorinated and aromatic hydrocarbons, in mixtures of aromatic and aliphatic hydrocarbons, and in many ketones, esters, and glycol ethers.

They may be cold-blended or copolymerized with a variety of other resins as described later. They are resistant to acids, alkalis, water, corrosive atmospheres, greases, and oils.

Silicone resins require baking at elevated temperatures (300–500 °F [149–260 °C]) to develop their optimum film properties, and they are capable of thousands of hours of service at such temperatures. The decomposition temperature for most silicone resins is around 650 °F (343 °C). However, when pigmented with heat-resistant pigments such as aluminum or zinc, they afford protection against weathering and corrosion at operating temperatures up to 1000 °F (538 °C). The silicone resin will gradually volatilize on prolonged heating at this temperature, but a silica matrix remains which holds the pigment in place. Incorporation of ceramic frits into the formulation permits even higher operating temperatures—to 1400 °F (760 °C).

USES. Because of their exceptional heat resistance, the silicone resins find their main use in heat-stable maintenance coatings and industrial finishes for severe high-temperature applications such as hot stacks, oven walls, combustion engine mufflers, incinerator interiors, arc light reflectors, and wall and space heaters. Several Government specifications [58, 59, 60, 61] for high temperature-resistant paints are based on, or can be met by the use of, silicone resin vehicles. Although used primarily for their high temperature resistance, silicone resins also perform well at low temperatures. Applied from dilute solution to masonry surfaces, the silicones provide excellent water repellency. Some silicone fluids are used as additives in protective coatings to promote flow-out and prevent bubbling, and to produce hammertone finishes (sec. 4.1.4.5); these fluids should not be confused with the film-forming silicone resins.

3.9.2. Modified Silicone Resins

Where the maximum heat resistance obtainable with the pure silicone resins is not required, more economical yet heat-resistant coatings can be made with modified silicone resins that have been blended, or copolymerized, with organic resins such as alkyds, phenolics, epoxies, acrylics, amino resins, and cellulose derivatives. Both baking enamels and air-drying coatings are available. Suitable driers may be used in the baking types to permit lower baking schedules if necessary. In air-drying types, the organic constituent is usually the major component. As little as 25 percent of silicone resin can considerably increase the heat resistance and weatherability of organic resins that would quickly deteriorate if used alone. At the same time, some physical properties (e.g., adhesion, toughness, color, solvent resistance) may be enhanced by the organic resin.

3.9.2.1. SILICONE-ALKYDS.—Silicone-modified alkyd resins have been particularly useful in the coatings field. Baking enamels of this type combining a silicone with a non-drying oil alkyd retain their color and gloss for long periods of continuous service at temperatures up to 400 °F (204 °C). Air-drying aluminum paints based on silicone-modified medium-oil alkyds have excellent corrosion resistance and weatherability, and will withstand temperatures up to 800 °F (427 °C) for limited periods. Short-oil alkyds containing about 30 percent silicone have been used to make durable, gloss-retentive automotive finishes. Exterior trim paints having excellent chalk resistance can be made with silicone-modified long-oil alkyds. Heat- and corrosion-resistant primers for use on metals under silicone-modified topcoats are usually based on a silicone-alkyd vehicle with suitable heat- and corrosion-resistant pigments, such as zinc chromate, aluminum paste, or zinc dust (also see sec. 3.4.2.2).

3.9.2.2. OTHER SILICONE-MODIFIED RESINS that are the basis for durable coatings combining many of the desirable properties of each component include combinations of silicones with phenolic resins to produce weather- and water-resistant maintenance paints; with acrylic resins or melamine-formaldehyde resins for durable white enamels; with chlorinated rubber to make tough, heat- and corrosion-resistant industrial maintenance paints; with epoxy resins for strong, heat-resistant electrical insulating coatings; and with cellulose derivatives, such as ethyl cellulose and cellulose nitrate, to make heat- and weather-resistant lacquers.

3.10. Epoxy Resins

Epoxy resins, since their introduction in 1949, have found important and steadily increasing use in the coatings field because of their unsurpassed combination of excellent adhesion, toughness, and chemical resistance. They are the condensation products of epichlorohydrin with *bis*-phenol. The chain structure consists only of carbon-to-carbon and ether linkages and is therefore quite stable, with a considerably greater degree of chemical resistance than is obtained with ester linkages. Epoxy resins have two types of reactive groups, the terminal epoxide groups and the hydroxyl groups along the polymer chains. They are therefore readily crosslinked with heat-reactive resins or polyfunctional amines to form

highly resistant, thermoset polymers. The hydroxyl and epoxide groups may also be reacted with organic acids; esterification with long-chain fatty acids such as linseed, soy, or cocoanut fatty acid yields alkyd-like resins with the inherently more stable ether linkage of the epoxy chain as the backbone instead of the ester linkage of the alkyd.

Because of the wide spacing between the reactive epoxide and hydroxyl groups, even the crosslinked epoxy polymer retains an unusual degree of flexibility along with its strength and chemical stability. Etherification of the chromophoric phenolic hydroxyl group during the condensation with epichlorohydrin greatly reduces yellowing tendencies in the epoxy polymer. The polar nature of the epoxy molecule accounts for its strong adhesion to a wide variety of surfaces. It also accounts for its solubility in oxygenated solvents such as ketones, esters, and ether-alcohols and in chlorinated hydrocarbons. Aromatic hydrocarbons and alcohols are latent rather than active solvents for epoxy resins.

The various grades of epoxy resins offered commercially differ primarily in molecular weight, the solubility and compatibility usually decreasing with increasing molecular weight. In general, the epoxies are compatible with pure phenolic resins, urea-formaldehyde resins, chlorinated biphenyls, and polyvinyl formal. They are incompatible with rosin-modified phenolics, cellulose derivatives, and most alkyds. The lower molecular weight epoxies are compatible with polyvinyl acetate and have limited compatability with a few natural resins and ester gums.

From the standpoint of composition and use, the epoxy resins fall into three categories: (1) unmodified (unesterified) baking types, (2) unmodified (unesterified) air-drying types, and (3) esterified types for either air-dry or baking finishes. These are discussed below.

3.10.1. Unmodified Epoxy Baking Resins

The maximum adhesion, durability and resistance properties of the epoxies are realized with the higher molecular weight, unmodified (unesterified) epoxy baking resins. These are dissolved in suitable solvents and blended with certain urea-formaldehyde or phenol-formaldehyde resins. Upon baking, they cure to tough, hard, thermoset coatings that exhibit outstanding adhesion, flexibility, and chemical resistance (especially to alkalis). These coatings find extensive use in applications such as corrosion- and abrasion-resistant tank and drum linings, can coatings, appliance primers, refrigerator and washing machine finishes, hospital furniture, collapsible tube linings, wire enamels, clear metal finishes, and industrial finishes for equipment that must withstand corrosive atmospheres. Thick epoxy coatings can be applied to irregularly shaped objects and grill-work by the fluidized resin bed technique (see sec. 5.4.6).

3.10.2. Unmodified Epoxy Air-Dry Resins

The amine-cured epoxy resins combine most of the advantageous properties of a baked film with the convenience of an air-dry coating. Reactive amines, such as ethylene diamine or diethylene triamine, reduced with a suitable amount of thinner, are stirred into the vehicle shortly before use at a concentration of about 6 to 8 parts per hundred parts (by weight) of resin. Once the amine hardener has been added, the pot life of the mixture is from 8 to 60 hours depending on the nature of the resin and the amine used. Where possible, an induction period of a half-hour to an hour should be allowed after mixing before applying the coating [62]. Because of the caustic, volatile, and toxic nature of reactive organic amines, care must be exercised to avoid contact with the skin and to provide adequate ventilation during their use. The lower molecular weight epoxy resins are well suited for cold-curing applications. Their better solubility permits a high solids vehicle which can be applied in a heavy coat in one operation. Since curing proceeds by direct crosslinking rather than by oxidation, thick coats are evenly hardened throughout without difficulty, provided the substrate is porous enough to permit escape of solvent. On nonporous surfaces, thickness should be limited to about 2 mils and sufficient time (1 to 2 days) should be allowed before over-coating, to avoid entrapment of solvent that might migrate to the interface and impair adhesion. The cured coating is almost colorless and is satisfactory for white and pastel finishes as well as for deep colors and clear coatings.

The amine-catalyzed cold-cured epoxy resins possess very good chemical resistance, toughness, and durability and are finding increasingly greater use in industrial maintenance paints, architectural paints and enamels, spar varnishes for marine applications, and clear coatings for floors, furniture, concrete, and metal. They may be applied by brush, spray, or flow-coating methods. For spray application a special type of spray gun [63] is available which mixes the resin and hardener in the head of the gun at the instant of use (see sec. 5.4.3.6).

Epoxy-polyamide coatings are discussed under Polyamide Resins (sec. 3.11.3).

3.10.3. Esterfied Epoxy Resins

Epoxy resins can be esterified by reaction with fatty or rosin acids in heating kettles.

in a manner somewhat similar to that by which alkyd resins are made. By the use of different types and amounts of organic acid, a variety of air-dry or bake-type vehicles can be prepared. The baking types are often blended with amino resins to improve their chemical resistance. The epoxy esters are less expensive and more widely soluble and adaptable than the unmodified epoxy resins, but they are not as chemical- or weather-resistant. They soon chalk on outdoor exposure, but their ultimate film life is greater than that of medium-length alkyds, and they have better resistance to mildew and dirt collection.

Where the maximum chemical resistance obtainable with the unmodified epoxies is not required, the epoxy esters offer a very useful combination of adhesion, flexibility, toughness, and durability for coatings applications. Long-oil epoxy esters find use in air-dry furniture and floor finishes, trim and trellis paints, and general-purpose interior and exterior enamels. Short-oil baking types combined with urea- or melamine-formaldehyde resins are used for appliance finishes, industrial baking enamels and primers, metal cabinet enamels, and decorative enamels.

Styrenated epoxy ester resins can be prepared by adding styrene monomer to the partially esterified epoxy ester and refluxing the mixture. The resulting resins, while somewhat similar to styrenated alkyds, are superior to the latter in outdoor durability, chemical resistance, and mar resistance. They find use in fast-baking enamels, force-dry wood finishes, and quick-drying varnishes.

3.11. Polyamide Resins

Polyamide resins are the polymeric condensation products of dibasic organic acids and polyamines, with recurring amide groups as an integral part of the main chain. Although the different polyamides constitute a large family, those of chief importance are of three types: (1) the nylons, (2) thermoplastic fatty acid-diamine polymers, and (3) thermosetting fatty acid-polyamine polymers. These types are discussed below.

3.11.1. Nylon Resins

The nylon resins are linear polyamides made by the condensation of di-carboxylic acids with diamines. They are capable of being formed into strong, oriented filaments on stretching. The oldest and most widely used type of nylon is that based on adipic acid and hexamethylene diamine (called nylon 6/6 because both the acid and amine components have six carbon atoms). Another major type is nylon 6/10, in which sebacic acid is used instead of adipic acid to yield a softer, more flexible polymer with lower water absorption and greater stiffness at high humidities. A newer type, nylon 6, is made by heating caprolactam (a six-carbon ring-type amide) under conditions in which the ring opens to form a linear polymer; this type has a lower softening temperature and a wider solubility than the other types of nylon.

Although the nylons are thermoplastic resins, their heat-distortion temperature (about 270-360 °F [132–182 °C]) is considerably higher than that of most other thermoplastic resins and many thermosetting ones. In addition to their heat resistance, they have fairly good resistance to sunlight (although they yellow slightly), and they are resistant to weak and strong alkalis, dilute acids, and most organic solvents. Among the very few good solvents for ordinary nylons (nylon 6/6 and 6/10) are phenol, *m*-cresol, and formic acid. Nylon 6 is soluble also in aqueous isopropanol and higher alcohols. Nylon resins are strong, tough, and abrasion-resistant. Their low coefficient of friction gives them excellent wear resistance even in the absence of lubrication. The excellent combination of properties possessed by the nylon resins has led to their wide and important use as a textile fiber and for molded plastic articles and mechanical parts. However, they have found only limited use in the coatings field because of their poor solubility and high softening temperature. Nylon 6, because of its wider solubility and lower softening temperature, is finding use in both solution and dispersion form as a coating for textiles, leather, wire, and heat-sealing foils.

3.11.2. Thermoplastic Polyamides

Linear, thermoplastic polyamide resins can be made by the condensation of dimerized fatty acids with diamines (e.g., ethylene diamine). Unlike the nylons, these are fairly soluble and compatible with a variety of solvents, plasticizers, and resins. Combinations of alcohols and aromatic hydrocarbons are the best solvents. They are soluble also in isopropanol and higher alcohols, in hot aromatic hydrocarbons, in chloroform, and in acetic acid. They are not soluble in glycols, aliphatic hydrocarbons, ketones, or esters. They are compatible with phenolic, maleic, and rosin resins, but are incompatible with most vinyl resins, urea- and melamine-formaldehyde resins, petroleum resins, coumarone-indene, and cellulose derivatives. Although they may be blended and are to a limited extent reactive with epoxy resins, the more reactive, thermosetting types of polyamide are more often used for this purpose, as discussed later.

The properties of the various polyamide resins can be varied over a wide range of flexibility and hardness by blending with each other or with various liquid plasticizers or compatible resins. Polyamide coatings offer a good combination of properties, including toughness, water and chemical resistance, grease resistance, good electrical properties, and excellent adhesion to a variety of surfaces, including difficult ones such as cellophane, glassine, and polyethylene. They are useful as heat-sealing coatings for paper, fabrics, metal foils, and many plastics. They also find use in high gloss, overprint varnishes and lacquers, and in lacquer-type printing inks. A recent and increasingly important use for the thermoplastic polyamide resins is in the formulation of thixotropic paints; for this purpose, they appear to be superior to the metallic stearates and soap solutions used in the past. The polyamides also make good general-purpose adhesives. Polyamide coatings may be applied as a hot melt, from solution, or as an aqueous dispersion.

3.11.3. Thermosetting Polyamides

The thermosetting polyamide resins are the polyfunctional condensation products of dimerized fatty acids with polyamines (e.g., diethylenetriamine). They range from soft, tacky resins to pourable fluids. They may be reacted with epoxy, phenolic, or other resins to produce thermoset resins with very useful properties.

3.11.3.1. EPOXY-POLYAMIDE RESINS are of particular importance. They are obtained by blending reactive polyamide resins with epoxy
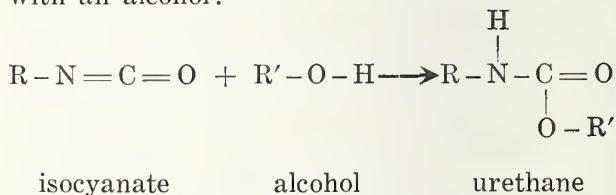
resins, the polyamide serving as both curing agent and modifier for the epoxy resin. The resulting resin blend yields coatings having excellent gloss, hardness, flexibility, impact resistance, and abrasion resistance, plus very good resistance to solvents, chemicals, and outdoor weathering. They are superior to straight epoxies in resistance to continuous water immersion. Although resembling amine-cured epoxies in their ability to cure at room temperature without requiring oxygen, the epoxy-polyamides have a considerably longer pot life. In many cases they may be applied as soon as mixed without the induction period recommended for epoxy resins. Epoxy-polyamide coatings exhibit outstanding adhesion to almost any type of surface—metals, plastics, glass, paper, fabrics, leather, wood, ceramics, rubber, masonry, etc. Effective corrosion-inhibiting primers using zinc chromate pigment can be made with epoxy-polyamide vehicles provided the pigment is dispersed in the epoxy resin before adding the polyamide. The epoxy-polyamides also make very good vehicles for zinc-rich paints (see sec. 2.3.1.5). Epoxy-polyamides are used as chemical-resistant can coatings, drum and pipe linings, weather- and water-resistant marine finishes, abrasion- and corrosion-resistant coatings for industrial equipment, floor coatings, and in many other applications where their combination of excellent adhesion, toughness, and chemical resistance are utilized to advantage. Several Military specifications for epoxy-polyamide coatings are cited in the bibliography of chapter 8 [129, 130, 131, 132].

In addition to their usefulness in the coatings field, epoxy-polyamide resins also find use as general adhesives, as plastic solders and sealants, and in casting, potting, and laminating applications.

3.12. Polyurethanes

The polyurethanes are among the most recent and promising resins to achieve prominence in the coatings field. First developed in Germany during World War II, the knowledge was transferred to the United States in 1945, and manufacture of the necessary diisocyanate raw materials started in this country in 1950. Since 1954, with the establishment of several large companies for the manufacture and development of polyurethane resins, the use of this versatile class of polymers has grown steadily, with applications in the fields of flexible and rigid foams, elastomers, synthetic fibers, adhesives, and coatings.

The fundamental urethane reaction, discovered by Wurtz in 1848, is that of an isocyanate with an alcohol:

$$R-N=C=O \ + \ R'-O-H \longrightarrow R-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\underset{\displaystyle O-R'}{|}}{C}=O$$

isocyanate   alcohol   urethane

The active hydrogen atom of the hydroxyl group is transferred to the nitrogen atom of the isocyanate group, while the alcohol residue

(alkoxy group) becomes attached to the carbon atom of the isocyanate group. In the general urethane reaction, the active hydrogen atom can be furnished by any hydroxyl-bearing compound, including castor oil polyols, carboxylic acids, water, and selected polyesters and polyethers—or by analogous compounds in which the active hydrogen is attached to a nitrogen or sulfur atom instead of an oxygen atom. Through the reaction of polyfunctional isocyanates (usually toluene diisocyanate) with polyols, either linear or crosslinked polymers can be formed, depending on the functionality and ratio of the reactants. The properties of the polyurethane are dependent also on the structure of the polyol employed; for example, a simple triol such as glycerol will yield a hard, brittle polymer, while a castor polyol or a polyester, with greater spacing between hydroxyl groups, will yield a flexible polymer. The ultimate film properties are affected also by the solvent system employed and by the curing temperature and humidity. Since isocyanate groups are reactive with water and hydroxyl-bearing materials, care must be exercised to use solvents which are water- and alcohol-free. Pigments, fillers, and dyes also must be chosen with care if good package stability is to be maintained.

The combination of different isocyanates with the large number of available polyols, in various NCO/OH ratios, makes possible the formation of a wide variety of polymers with properties "tailored" to specific applications. Polyurethane coatings formulated for optimum performance are characterized by an outstanding combination of desirable properties, including hardness with flexibility, high gloss, and excellent resistance to abrasion and chemicals. They may be applied by dipping, knife, or spray.

Polyurethane coatings are available either as two-component systems that are mixed shortly before use and cure by direct crosslinking, or as single-package materials that cure when exposed as a film to moisture, oxygen, or heat. The reaction between isocyanate groups and active hydrogen atoms proceeds readily at room temperature without catalysts; however, the reaction is greatly accelerated by the addition of small amounts of tertiary amines, sodium alkoxides, or Friedel-Crafts catalysts, or by heating. The two-component polyurethane systems at present provide the maximum versatility and best properties obtainable with this class of resins, although continuing research on one-component and on solventless systems may change this situation.

3.12.1. Two-Component Urethane Systems

Two-component polyurethane coating systems are of two types: a so-called Prepolymer type, and a so-called Polyisocyanate type. Both are formulated for room temperature cure, but curing may be hastened and hardness and toughness of the coating increased by baking.

3.12.1.1. The PREPOLYMER TYPE of vehicle consists of isocyanate-terminated polymers together with a substantial proportion (about 2-15%) of free toluene diisocyanate (TDI), the usual isocyanate raw material. Since TDI is very volatile and highly toxic, such prepolymer vehicles retain some toxicity until cured. Curing is accomplished by mixing the prepolymer with polyfunctional, reactive amines and polyols shortly before use. The pot life of the mixed ingredients and the time required for the coating to cure depend on the nature and concentration of the curing agents and on the temperature. Normally, a pot life of 8 hours or more can be expected. The usual polyurethane prepolymer coatings dry in an hour or two and may be recoated in four to six hours. Maximum hardness and resistance properties are developed in about a week.

3.12.1.2. The so-called POLYISOCYANATE TYPE is a prepolymer that has been specially processed to produce a largely tri-functional polymer with little if any residual, unreacted TDI. Since there is virtually no free TDI in such vehicles, their toxicity is no longer a problem. They are cured by mixing with suitable reactive polyols, including the castor polyols, and various hydroxyl-bearing polyethers and polyesters [146]. To a lesser extent, polyamines are used to effect the curing. Depending on the nature of the polyol and the drying conditions, about 2 to 15 hours may be required for drying. As with all polyurethanes, the properties of the final coating are determined largely by the nature of the modifying polyol; that is, by the number and spacing of hydroxyl groups in the polyol. As has already been pointed out, either linear, branched, or crosslinked polymers can be obtained, depending on the functionality and ratio of the reactants. As a matter of convenience in mixing and use, the proportioning of the polyisocyanate prepolymer and polyol curing agent can readily be worked out in advance by the manufacturer to permit the mixing of equal volumes of polyisocyanate and polyol on the job for optimum results.

3.12.2. Single-Package Urethane Systems

Single package polyurethane coating systems are formulated to cure by application of heat, by oxidation, or by reaction with atmospheric moisture.

3.12.2.1. HEAT-CURED one-package polyurethane vehicles can be prepared by temporarily

blocking the reactivity of the -NCO groups in a polyisocyanate prepolymer by loosely associating them with a reactant (e.g., phenol) that is driven off at elevated temperatures. While the isocyanate groups are blocked off at room temperature, suitable polyol or amine curing agents may be added which will not be effective until the composition is heated to reactivate the isocyanate groups. Such heat-cured systems have been particularly useful as wire coatings that permit soldering without the need for stripping the insulation.

3.12.2.2. AIR-CURED one-package polyurethane vehicles may appropriately be termed urethane-alkyds, since they are made—like alkyd resins —by cooking together a polyol and a drying oil, with toluene diisocyanate as the other major reactant instead of phthalic anhydride. Such vehicles are sometimes called urethane oils. They dry by oxidation of the carbon double-bonds in the drying oil and hence require the use of ordinary amounts of conventional paint driers in order to cure within a reasonable length of time. The performance of such coatings is quite similar to that of conventional alkyds.

3.12.2.3. MOISTURE-CURED one-package polyurethane vehicles utilize the ready reactivity of isocyanate groups with water to effect cure of the coating. The functionality and molar ratios of the reactive ingredients are important factors in the successful formulation of such vehicles. The reaction between water and isocyanate first produces an amine and carbon dioxide gas. The amine reacts with more isocyanate and gradually builds up a polymeric structure, while the carbon dioxide gas diffuses out of the film. The cured film has properties approaching those of the two-component systems, but the rate of cure depends on the prevailing weather conditions. In a typical one-package system, the film is laid down from a water-free solution of an isocyanate prepolymer in organic solvents. The film dries tack-free

in about an hour by solvent evaporation and then cures by reaction with atmospheric moisture to a crosslinked coating. Recoating is usually possible in four to six hours, and optimum film properties are developed in about a week, as with the two-package systems. However, under low humidity conditions (below 30% R.H.) longer curing times may be required.

3.12.3. Properties and Uses of the Polyurethanes

It has been stated that a wide variety of polyurethane coatings for particular applications is possible, depending on the nature of the reactants employed. For example, by varying the molecular weight of the polyol (and hence the distance between cross-links), extremely hard or soft flexible polymers can be obtained. Tough polyurethane coatings combining hardness with flexibility can be prepared which are well-suited as floor varnishes for severe service, such as on gymnasium floors, and as porch and deck enamels on wood or concrete. Their excellent mar and abrasion resistance is also utilized in furniture finishes. A polyurethane coating [147] for use on polyester-fiberglass gunstocks over a polyamide-epoxy primer [148] is covered by Mil. Spec. MIL–P–46057. Their water and corrosion resistance makes them useful for marine paints and for metal primers and enamels. Their weather resistance is utilized in clear varnishes for boats and exterior wood siding (the polyurethanes do not adhere satisfactorily to oil based wood fillers and stains but adhere well to alcohol- or water-based stains and fillers). The excellent alkali resistance of the polyurethanes finds use in masonry coatings and swimming pool paints. Although polyurethane coatings tend to darken somewhat on exterior exposure, they have excellent gloss and gloss retention in applications where prolonged decorative as well as protective qualities are desired. The polyurethanes are still relatively expensive materials but are becoming cheaper as their volume of use steadily grows.

3.13.   Polyethylene

The outstanding properties of polyethylene are its chemical inertness, solvent resistance, flexibility, toughness, excellent dielectric and related properties, and low cost. Although its widest use is in the form of film, sheet, and molded articles—its coatings applications being limited by its complete insolubility in organic solvents at room temperature—the excellent properties of the resin have been utilized in the coatings field by employing hot melt or flame-spraying methods (sec. 5.4.3.4), a fluidized resin bed technique (see sec. 5.4.6 on Methods of Application), or water-dispersed

systems to effect coatings application. Though generally inert, polyethylene is attacked by halogens and concentrated nitric acid and is soluble in hot aromatic hydrocarbons. It is resistant to other mineral acids including hydrofluoric, and is unaffected by strong caustic.

3.13.1. Low- and High-Density Polyethylene

Polyethylene is prepared by the addition polymerization of the ethylene monomer. The properties of polyethylene, like all polymers, vary with molecular weight and structure and

with molecular weight distribution. In the case of polyethylene, an additional parameter, density, is an important factor in determining the properties of the material. The density of polyethylene may range from 0.92 (g/cc) in the older, conventional, low-density type to 0.96 in the newer, linear, high-density type. Conventional polyethylene is made by a high-pressure process, usually by mass polymerization, but sometimes by a "solvent" or slurry process; the resulting polymer has a branched structure which reduces the tendency toward crystallization, the degree of crystallinity being about 60-65 percent. The new, linear type of polyethylene is virtually free from branching, so that greater alignment and close-packing of polymer chains is possible, and this type has a degree of crystallinity of 80-85 percent; it is manufactured by a low-pressure process of solution polymerization employing the new stereospecific catalysts (see sec. 3.1.4.5 on Stereoregular Polymers). The greater crystallinity of linear polyethylene gives it a higher density, a higher melting point, greater impermeability to moisture and gases, greater stiffness and tensile strength, and greater solvent and chemical resistance than is possessed by the conventional, low-density type. Molecular weights as high as 2,000,000 can be achieved in high-density polyethylene, whereas a molecular weight of about 50,000 is the highest practically obtainable in the conventional type.

A medium-density polyethylene with properties intermediate between those of the low- and the high-density types is also being manufactured, by both the high- and the low-pressure processes with recently-developed modifications. All three types of polyethylene (high-, medium-, and low-density) are readily melted, molded, extruded, or heat-sealed. The heat-sealing temperature for the linear, high-density type is about 50 °F (28 °C) higher than that of the conventional, low-density type.

Since the cost of high-density polyethylene is greater than that of the low-density type, the choice of type is dictated by the requirements of the application. For example, where a high degree of impermeability is desired, a medium-density material is greatly superior to the low-density type, but the degree of impermeability is not much increased by further increasing the density. On the other hand, where maximum hardness and heat resistance are required, a high-density polyethylene will give the best results.

USES. The most important application for polyethylene in the coatings field is in packaging. Extruded in a thin film onto a moving sheet of paper, aluminum foil, or other packaging material, it provides a clear, strong, flexible, abrasion-resistant, heat-sealable coating of low permeability that is highly resistant (except at elevated temperatures) to strong acids (except concentrated nitric) and alkalis, solvents, greases, and oils. Polyethylene-coated aluminum foil is heat-sealable and completely moisture-proof. Polyethylene-coated cellophane and polyester film are finding increasing acceptance. Cardboard cartons for milk and other liquids are being coated with polyethylene; plasticizers and other modifiers are unnecessary in polyethylene, and it is odorless, tasteless, and nontoxic. Polyethylene is extruded onto fabrics to make them waterproof. Nonwoven mats of cellulose fibers coated with polyethylene are used to make disposable baby diapers and hospital sheets. Irregularly shaped metal parts can be coated with polyethylene by a fluidized-bed technique (see sec. 5.4.6). A heavy coating of polyethylene can be applied to metal surfaces by flame-spraying (see sec. 5.4.3.4); thus, tough chemical- and abrasion-resistant coatings can be applied to chemical storage tanks, metal bench tops, drums, and pipe. The excellent electrical properties of polyethylene are utilized in coatings for wire and cable.

For elevated temperature or outdoor applications, polyethylene must be stabilized against oxidation. Effective stabilizers are available. Carbon black is a particularly effective light stabilizer for polyethylene subjected to exterior exposure. Heat stabilization is accomplished by incorporation of an antioxidant.

3.13.2. Irradiated Polyethylene

Polyethylene can be crosslinked by a few seconds exposure to sufficiently intense high-energy radiation. By regulating the radiation dose, the degree of crosslinking can be controlled so that the melting point of the resin is raised as much as 50 °F (28 °C) above that of normal polyethylene without greatly altering its basic mechanical properties. Very high dose levels will render the resin infusible at temperatures up to the decomposition point. It is interesting to note that the increase in softening temperature induced in conventional polyethylene by irradiation is about the same as that achieved in going from low-density to high-density polyethylene. The high-density material also can be improved by irradiation.

3.13.3. Chlorosulfonated Polyethylene

Chlorosulfonated polyethylene is an elastomeric material produced by the simultaneous chlorination and sulfonation of already-polymerized relatively high molecular weight low-density polyethylene, by treatment with gaseous chlorine and sulfur dioxide in the presence of a free-radical initiator (e.g., a peroxide) as catalyst. The chlorine atoms reduce the crystallinity (and hence the stiffness) of the polyethylene

without greatly changing its desirable properties. The sulfonyl chloride groups provide reactive sites through which subsequent cross-linking (vulcanization) can take place. By varying molecular weight, chain branching, and degree of crystallinity and cross-linking through control of chlorine and sulfur content, a variety of chlorosulfonated polyethylene derivatives can be prepared. The product offered commercially is usually derived from a polyethylene having a molecular weight of about 20,000, and contains about 27 percent chlorine and 1.5 percent sulfur. Curing is effected through the sulfonyl chloride groups by employing curing systems based on a polybasic metal oxide or metal salt of a weak acid (e.g., litharge or magnesia), an organic acid, and an organic accelerator. The cured polymer has excellent resistance to abrasion, heat, weathering, and cracking, and is completely resistant to ozone; it has good resistance to mineral oils and to corrosive chemicals such as oxidizing acids, alkalis, chrome plating baths, and hydrogen peroxide. The litharge-cured coating systems have good resistance to prolonged water immersion, but the magnesia-cured systems are inferior in this respect.

Solution coatings of chlorosulfonated polyethylene can be formulated in a variety of colors, including white. They can be applied to virtually all other elastomeric compositions to provide protection against weathering and ozone. The coatings may be used without curing if a light stabilizer and detackifying resin are incorporated into the formulation. However, a heat cure is required for maximum resistance properties. Coatings that will cure at room temperature can be prepared by using special accelerators. Unpigmented lacquers based on chlorosulfonated polyethylene can be applied to rubber sporting goods and footwear to provide a durable, lustrous, protective finish. Cotton and synthetic fabrics coated with this resin exhibit excellent weathering resistance. Chlorosulfonated polyethylene coatings are proving useful in rugged service applications such as upholstery fabric, awnings, tarpaulins, heavy duty gloves, and as industrial maintenance coatings in corrosive [141] or abrasive environments. Coatings of chlorosulfonated polyethylene have excellent adhesion to chlorinated rubber-primed [140] sandblasted steel. They may also be applied to wood and masonry surfaces. (See also sec. 3.15.2).

3.14. Fluorocarbon Resins

The fluorocarbon resins are substituted ethylene plymers in which hydrogen atoms have been replaced with fluorine atoms or both fluorine and chlorine atoms. The resulting polymers are characterized by their chemical inertness, low coefficient of friction, heat resistance, and strength and flexibility over a wide temperature range. Of chief interest are polytetrafluoroethylene and polychlorotrifluoroethylene.

3.14.1. Polytetrafluoroethylene

Polytetrafluoroethylene is a completely fluorinated, linear polymer having a dense, symmetrical, highly crystalline structure that is completely resistant to chemical attack by all known substances except molten alkali metals, and fluorine at high pressures. It is the most heat-resistant organic polymer known, being capable of continuous service at temperatures up to 500 °F (260 °C). Although it is thermoplastic and softens at about 620 °F (327 °C), it does not melt, and at about 750 °F (399 °C) it decomposes slowly to yield the monomer and lesser amounts of various gaseous fluorine derivatives. The decomposition products are dangerously irritating and toxic and should not be inhaled. Small amounts of gaseous decomposition products are given off also at the sintering temperature (650 °F [343 °C]) to which the resin particles as manufactured must be heated to fuse them into a continuous mass. The resin is available in the form of granules for compression molding, as a powder for extrusion molding, and as an aqueous dispersion for coatings applications; in each case, fusion of the resin particles is achieved by sintering as indicated above.

Polytetrafluoroethylene has a translucent, white, or grayish color, and a waxy feel. Nothing will stick to the untreated surface; however, the surface can be dulled by treatment with a molten sodium-ammonia mixture and thus rendered capable of being bonded with various commercial adhesives. Polytetrafluoroethylene has a very low coefficient of friction—the lowest of all known solids—and the static coefficient is lower than the dynamic coefficient; thus, bushings made of or coated with the resin exhibit smooth, non-binding motion and long wear without the need for lubrication. Polytetrafluoroethylene retains its good strength and flexibility over a very wide temperature range, from −150 to 500°F (−101 to 260°C), and it has very high impact strength. It is nonflammable. Its water absorption is practically zero. It has a specific gravity of about 2.2. Although possessing excellent stability, it exhibits some cold flow (non-elastic, permanent deformation

under stress) at moderately elevated temperatures, the heat distortion temperaure for the bulk material beging 250 ° F (121 ° C) at 66 psi.

The electrical properties of polytetrafluoroethylene are outstanding. It has a very low dielectric constant and very low dissipation factor which remain virtually unchanged in the frequency range from 60 cycles to 10,000 megacycles. Dielectric strength and arc resistance are excellent.

To attain in a coating the maximum performance properties of which polytetrafluoroethylene is capable, it is necessary that the coating be free of pinholes. Since the resin does not melt or flow during the fusion process, pinholes are likely to be present unless multiple coats (at least three) are applied.

Despite its high cost, the unique combination of desirable properties possessed by polytetrafluoroethylene makes its use both practical and economical for severe applications in which maximum chemical resistance and heat stability are required. Aside from its uses in molded, machined, and extruded forms, polytetrafluoroethylene in the form of dispersion coatings may be applied to metals, glass, ceramics, wire, fabrics, and mats. Sintering at about 650 °F (343 °C) fuses the particles into a continuous, tough, extremely resistant film that can be used in such applications as a lining for corrosive-reaction vessels; as a chemical-resistant coating for drums and tanks; as a protective coating on machinery and equipment subjected to heat, fumes, and spillage; as an anti-adhesion coating on processing equipment and moving parts subject to clogging and misfunction as a result of undesired buildup of materials (e.g., buildup of glue on packaging machines); as a low-friction, wear-resistant coating for machine parts that cannot be lubricated; and as an insulating coating for wire and electrical parts for severe or critical electronic applications.

3.14.2. Polychlorotrifluoroethylene (Kel-F)

Polychlorotrifluoroethylene is a completely halogenated, linear polymer containing, on the average, one chlorine atom for every three fluorine atoms. The fluorine imparts chemical inertness, thermal stability, and almost zero water absorption to the polymer, while the chlorine—in part by reducing molecular regularity and crystallinity—contributes a lower softening temperature, meltability and moldability, reduced cold-flow, and greater transparency. The degree of crystallinity depends on the temperature treatment received during the manufacturing process; quick quenching of the heated polymer yields a relatively amorphous material with much smaller crystallites, while slow cooling produces a more crystalline polymer. Molecular weight also can be varied

to produce polymers ranging from low molecular weight oils, greases, and waxes to high molecular weight (300,000 to 400,000) molding and dispersion resins.

Although not as extremely inert and thermally stable as polytetrafluoroethylene, polychlorotrifluoroethylene finds many similar uses. It is resistant to all corrosive chemicals (including fuming oxidizing acids) except molten alkali metals, fluorine, and highly halogenated compounds. It is insoluble in all organic liquids at room temperature, but is swelled slightly by halogenated solvents, toluene, diethyl ether, and ethyl acetate. At elevated temperatures, it is swelled by still other liquids and can be dissolved by a few, such as highly halogenated compounds. The softening temperature of the molding and dispersion resins may vary from about 350 to about 420 °F (177 to 216 °C), depending on their molecular weight and degree of crystallinity. Polychlorotrifluoroethylene is capable of continuous service at temperatures up to 400 °F (204 °C), while retaining an appreciable degree of flexibility at temperatures around —200 °F (—129 °C) or lower. It is resistant to weathering and aging, and is nonflammable, strong, tough, and abrasion-resistant. It has greater resistance to cold-flow than the tetrafluoro polymer. Its electrical properties are excellent; it combines high dielectric strength and arc resistance with a low dissipation factor (the latter is not as low, however, as that of polytetrafluoroethylene, polyethylene, and polystyrene).

For coating purposes, dispersions of finely divided polychlorotrifluoroethylene in volatile organic solvents are generally employed. These resins may be applied by spraying, spreading, or dip-coating to metals, ceramics, glass, wire, and certain fabrics and other materials. Special primers are available to increase adhesion where necessary. After evaporation of the organic solvent the coating is fused by heating to the melting point to form a tough, permanent, continuous film that has all the properties of the basic resin. Since the resin actually melts and flows during the baking process, a pinhole-free coating can be obtained. Despite the high cost of polychlorotrifluoroethylene resins, they are widely used as corrosion- and chemical-resistant coatings for metals in severe industrial applications where their exceptional resistance properties provide long-term savings in maintenance and replacement costs. Typical industrial applications include coatings for troughs, tanks, vats, hoppers, mixers, paddles, pumps, and conveyors. Fabrics coated with the resin are rendered waterproof and resistant to heat, chemicals, fungi, weathering, and abrasion, while retaining flexibility at very low temperatures.

3.15. Synthetic Rubbers

Synthetic rubbers, in addition to their usefulness as substitutes for natural rubber, also find important uses as adhesives, and in coatings where resilience, abrasion resistance, distensibility, and elasticity are of prime importance. Among the synthetic elastomers available are a number of materials which combine excellent heat, chemical, and weathering resistance along with their desirable elastomeric properties. Those of particular interest to the coatings field are discussed in the following sections.

3.15.1 Polychloroprene (Neoprene)

Neoprene is a tough, resilient material possessing outstanding resistance to oils, alkalis, heat, weathering, and abrasion. It will withstand continuous exposure to sulfuric and phosphoric acids and many other inorganic and organic acids, but is decomposed by very strong oxidizing compounds such as nitric and chromic acids, sulfur trioxide, and hydrogen peroxide. Neoprene is swelled and softened by aromatic and halogenated hydrocarbons, aromatic alcohols, esters, ketones (except acetone), turpentine, and carbon disulfide. It is very resistant to oils, aliphatic hydrocarbons, aliphatic alcohols, acetone, water, and most salts. Ethers and aldehydes, in general, have only a mild swelling effect on the polymer. Neoprene retains most of its desirable properties at temperatures as high as 150 °F (66 °C) and is serviceable at temperatures up to 250 °F (121 °C) for some applications. It remains flexible down to −20 °F (−29 °C), becoming brittle at lower temperatures. Long exposure to sunlight and weathering has little effect on neoprene; it tends to become hard and dry after long exposure, rather than soft and sticky as does natural rubber. Neoprene is virtually nonflammable.

Neoprene is prepared by the emulsion polymerization (see sec. 3.1.3.3) of chloroprene in an alakaline medium. The polymerization is halted when about 30 percent complete, while the polymer is still thermoplastic. The polymer is recovered by acidifying the emulsion to a point just short of coagulation and then freeze-coagulating the polymer onto a brine-cooled drum, from which it is stripped, washed, and dried. Several types of neoprene, differing in uncured properties and manner of cure, are manufactured. Also, several types are marketed in latex form. The partially polymerized polymer can be milled and compounded like raw rubber, and then vulcanized (crosslinked) by heat and/or catalysts to complete the polymerization. Although heat alone suffices to cure neoprene quite rapidly (in an hour or two) at temperatures around 270 °F (132 °C), accel-erators (basic metal oxides, such as magnesium oxide or zinc oxide) are generally employed to shorten the baking time or to lower the baking temperature. Satisfactory room-temperature curing neoprene coating formulations also have been developed and are commercially available.

Neoprene coatings are usually supplied as solutions of the uncured polymer in aromatic solvents. Catalysts or accelerators are added immediately prior to use. Heat-curing types are usually syrupy liquids that are best applied by brush or dip-coating, or they may be soft pastes that can be applied by troweling. Air-drying types may usually be applied by brush, dip, spray, roller, or flow. Depending on the nature of the formulation, thicknesses of 3 to 6 mils per coat are readily obtained by the aforementioned methods. Troweling yields coating thicknesses several times greater per coat. Where maximum protection, durability, and resilience are required (especially on sharply contoured surfaces), coatings up to $\frac{1}{4}$ inch in thickness can be obtained with multiple trowel coats. An adequate period (several hours) of air drying should precede baking to prevent blister formation from too rapid an escape of solvent. In general, neoprene coatings are utilized at thicknesses of 10 to 15 mils. A primer is required for maximum adhesion. Chlorinated rubber-base primers [140] have been very effective for this purpose. Neoprene coatings are generally available only in gray or dark colors, chiefly black and green.

Uses. The excellent combination of resistance and durability properties possessed by neoprene has been proved in many severe industrial applications since its introduction in 1932. Neoprene coatings are widely used to provide lasting protection against corrosion and abrasion of industrial equipment such as ductwork, pipelines, storage tanks, scrubber towers, tumbling drums, coal chutes, pump and blower blades, ship propeller shafts, tool handles, and machinery. Neoprene coatings may be applied to wood and concrete flooring, ramps, and steps to provide protection against wear and chemical splash or spillage; anti-skid properties can be imparted by incorporating grit or sand in the applied coating. Neoprene finds use as a chemical- and abrasion-resistant coating for textiles, rubber, and leather for such items as industrial gloves, heater and brake hose, belts, and conveyors. As a coating for ignition wire, neoprene affords excellent resistance to oil and heat. Neoprene coatings on military aircraft have exhibited excellent resistance to abrasion and erosion, although the weight of the thick coatings employed (about 10 mils) constitutes

somewhat of a drawback in aerodynamic applications. Neoprene coatings are widely specified maintenance finishes in oil refineries, chemical plants, garages, filling stations, and aircraft installations.

3.15.2. Chlorosulfonated Polyethylene

Chlorosulfonated polyethylene, was discussed previously in section 3.12.3 under Polyethylene. It may be useful here, however, to point out the considerable similarity between the properties and applications of chlorosulfonated polyethylene and those of neoprene, while indicating a basis for choosing between them. Both are highly suitable for applications in which resistance to heat, chemicals, weathering, and abrasion are required. Neoprene is less expensive than chlorosulfonated polyethylene and is superior in oil resistance. Chlorosulfonated polyethylene, however, possesses superior resistance to strong oxidizing agents such as nitric [141] and chromic acids, hypochlorite and chlorine dioxide solutions, hydrogen peroxide, and ozone —agents which soon deteriorate neoprene. It is available in a wide range of durable colors, both light and dark, whereas neoprene is limited to gray or dark colors. Also, chlorosulfonated polyethylene coatings are capable of service at higher temperatures than neoprene, the upper limit for continuous service being about 220 °F (104 °C) as compared with about 150 °F (66 °C) for neoprene. Neoprene, therefore, is the general-purpose material, while chlorosulfonated polyethylene is used where its specific superior properties justify the higher cost.

3.15.3. Styrene-Butadiene Rubber (SBR)

Styrene-butadiene copolymers of high butadiene content are soft, elastomeric materials, as distinguished from the harder, high styrene types usually used in the coatings field, predominantly in latex paints. The high styrene/low butadiene resins were discussed in section 3.8.2 under Styrene-Butadiene Copolymers. The styrene-butadiene copolymer elastomers usually contain about 75 percent butadiene; however, copolymers ranging all the way from 50 percent butadiene to 100 percent polybutadiene are manufactured, and are available both as solid polymers and as latexes. They are vulcanized with sulfur or sulfur-bearing materials. Although the chief use for styrene-butadiene copolymers is for SBR synthetic rubber (formerly called GR-S), they also find some use in coatings where their elastomeric properties are advantageous, as in coatings for rug backing, paper, fabrics, and leather. Such coatings are tough, flexible, abrasion-resistant, and acid- and alkali-resistant, but are attacked by aromatic and chlorinated hydrocarbons and are swelled by oils and greases. Styrene-butadiene rubber is also used in general-purpose adhesives.

3.15.4. Butadiene-Acrylonitrile Rubber (Nitrile Rubber)

The butadiene-acrylonitrile copolymers (nitrile rubbers) are similar to the butadiene-styrene rubbers in general appearance and physical properties, but nitrile rubbers have better resistance to most solvents (although they are soluble in ketones), greater resistance to the deteriorative effects of heat and sunlight, and excellent resistance to oils, greases, and waxes. The oil resistance increases with increasing nitrile content. Vulcanization is accomplished with sulfur or sulfur-bearing materials, as with butadiene-styrene rubbers. Nitrile rubbers have found use in the coatings field as nonvolatile, non-extractable plasticizers for phenolic resins and for polyvinyl chloride resins. In latex form, nitrile rubbers have been used as coatings and impregnants for paper, fabrics, and leather products.

3.15.5. Isobutylene-Isoprene Copolymer (Butyl Rubber)

Butyl rubber consists of about 98 percent isobutylene copolymerized with about 2 percent isoprene. The unsaturation imparted by the isoprene renders the copolymer vulcanizable, a property not possessed by 100 percent polyisobutylene. This degree of unsaturation is very low, however, compared to that found in natural rubber, and accounts for the chemical inertness of butyl rubber. Vulcanization, though more difficult than with diene polymers, can be accomplished with combinations of sulfur and thiuram accelerators or with special methylol-containing resins.

Butyl rubber is highly impermeable to gases (a property that has led to its wide use for automobile inner tubes). It has a "dead" feel, its resilience being strikingly lower than that of natural rubber.

Butyl rubber is highly resistant to concentrated acids and alkalis, corrosive salts, and fresh and salt water, and it has found use as linings for chemical tanks, pumps, and hoses. Its good electrical insulating properties coupled with heat resistance to about 212 °F (100 °C) and excellent resistance to aging and ozone make it useful as a wire coating. Because of its paraffinic hydrocarbon nature, it is resistant to esters, ketones, alcohols, animal fats, and vegetable oils, but it is attacked by petroleum hydrocarbons, aromatic hydrocarbons, chlorinated solvents, and carbon disulfide. It remains flexible at temperatures as low as −400 °F

(—240 °C), even after prolonged aging, and is proving useful in cryogenic applications. Its flexibility has made it useful as a coating for fabrics. Recently, efforts have been made to utilize the resistance of butyl rubber to aging, weathering, sunlight, and ozone in solution-type industrial maintenance coatings being offered for metal and masonry surfaces.

3.15.6. Polysufide Rubber

Organic polysulfide polymers result from the condensation of organic halides with alkali polysulfides. They range from viscous liquids to rubber-like solids. The polysulfide rubbers are processed and handled like natural rubber. Curing is accomplished with metallic oxides (usually zinc oxide). Polysulfide rubbers have excellent resistance to organic solvents, including most aliphatic and aromatic hydrocarbons, alcohols, ketones, and esters. Coatings based on polysulfide rubber have low permeability to gases, good electrical properties, excellent resistance to aging, sunlight, and ozone, and afford good protection against fresh and salt water. Their resistance to acids and alkalis is only fair. Although the tensile strength and abrasion resistance of polysulfide rubbers is generally lower than that of some other synthetic rubbers, specially formulated coatings based on polysulfide rubber exhibit excellent abrasion resistance. Blends of polysulfide rubber with vinyl resins have produced durable and useful coatings. Polysulfide rubber coatings have found use as solvent-resistant linings for chemical tanks and equipment, and as solvent-resistant coatings for paper, fabrics, leather, wood, and concrete.

3.15.7. Silicone Rubber

Silicone elastomers are high molecular weight, linear organosilicon polymers compounded with an inorganic filler and a vulcanizing agent (usually a peroxide). Recently, vinyl curing systems, involving the introduction of reactive pendant groups into the polymer and use of a specifically-reactive peroxide, have been developed. The general chemistry and properties of silicone resins have been discussed in section 3.9.1. Silicone elastomers are outstanding in their retention of flexibility over a wide range of temperatures, from —100 to 500 °F (—73 to 260 °C). Whereas most organic elastomers soon soften and deteriorate at temperatures above 200 °F (93 °C), the silicone elastomers are virtually unaffected by continuous service at a temperature of 300 °F (149 °C and will withstand a temperature of 600 °F (316 °C) for a brief period. Although very resistant to ozone and to hot oils, the silicone elastomers are poor in resistance to hydrocarbon solvents, and they are attacked by acids, strong alkalis, and steam. Their electrical properties and their resistance to weathering are excellent. Silicone rubber coatings are available as solutions, pastes, and water dispersions, for application by spraying, brushing, dip-coating, or spreading. They are applied to fabrics (including glass fabric), ceramics, asbestos paper, metals, and wire to provide resilient, flexible, durable coatings that retain their desirable properties over a very wide temperature range.

3.15.8. Polyurethane Rubber

The general chemistry and properties of the polyurethanes have been discussed in section 3.12. There it was noted that a wide variety of products can be made from the wide choice of polyols available. For the production of polyurethane elastomers, hydroxyl-bearing polyesters or polyethers are employed for reaction with the diisocyanate (usually toluene diisocyanate). Because of the wide spacing between reactive groups in such polyols, a flexible structure is produced. Polyurethane rubber possesses high tensile and tear strength and excellent abrasion resistance superior to that of the best cold rubber. Resistance to oxygen, ozone, and ultraviolet is excellent. Resilience and wear properties are outstanding. Optimum elastomeric properties, however, are not retained over a wide temperature range; polyurethane rubber hardens at moderately low temperatures (below —20 °F [—29 °C]) and weakens when subjected to high temperatures, steam, or hot water. Good resistance to solvents, alkalis, and acids can be built into the polymer. In addition to its uses as a premium specialty rubber and as a resilient, durable, foam or sponge rubber, polyurethane rubber is used as a coating to provide wear-resistant veneers on tires, soles, heels, belts, rubber and plastic goods, and flooring. Fabrics coated with polyurethane rubber are flexible, wear-resistant and weather-resistant.

3.15.9. Chlorinated Rubber

Chlorinated rubber (or Parlon®, as it is widely known in the trade) is prepared by the addition and substitution of chlorine atoms into the polyisoprene molecule to yield a material containing 63 to 67 percent chlorine. The chlorinated product is a thermoplastic resin rather than an elastomer and is used principally in coatings, inks, and adhesives. Chlorinated rubber is outstanding in its resistance to water and common corrosive chemicals. It possesses a high degree of impermeability to water vapor and a very low water absorption. It is highly resistant to strong alkalis and acids, strong bleaches, corrosive vapors and fumes [140], soaps and detergents, mineral oils, mold and mildew. It is deteriorated by heat and ultra-

violet light, but can be stabilized to improve its resistance to these influences. It is odorless, tasteless, nontoxic, and non-flammable.

Chlorinated rubber is readily soluble in chlorinated aromatic hydrocarbons and has found important use in corrosion-resistant paints and primers, industrial maintenance coatings, traffic paints, swimming pool paints [35], and concrete and masonry paints [34]. Other uses are in flame-retardant coatings, textile coatings, printing inks, and adhesives. Properly formulated chlorinated rubber coatings have proven very effective as adherent, corrosion-resistant primers for metals which are to receive neoprene topcoats. Paints, enamels, and lacquers based on chlorinated rubber are very quick-drying compared with most other film-forming materials.

3.15.10. Polyacrylic Ester Rubber

Polyacrylic ester rubbers are specialty polymers that can be cured with special vulcanizing agents, such as polyfunctional amines, to give products highly resistant to weathering, discoloration, ozone, and gas diffusion. Although resistant to many oils, even when hot, they are not resistant to aromatic solvents nor to glycols or steams. They are not well-suited for low temperature applications. In both solution and latex form, the polyacrylic ester rubbers are finding use in the coatings field.

3.15.11. Cyclized Rubber

Cyclized rubber is made by treating natural rubber with strongly acidic reagents (e.g., sulfuric or sulfonic acids) which reduce the original unsaturation through the formation of cyclic structures. The resulting product is hard, resinous, and thermoplastic instead of rubbery. While remaining soluble, like natural rubber, in hydrocarbon solvents, it is rendered much more resistant to water, acids, and alkalis. Cyclized rubber is supplied in the form of granules or powders that can be applied as hot melts or from solution in organic solvents to give adherent, flexible coatings having low water penetration and good chemical resistance. It finds use in coatings for paper and metals, in acid- and alkali-resistant paints, in printing inks, and as a strong metal-to-rubber adhesive.

3.16. Water-Soluble Resins

3.16.1. Thermoplastic Types

Several classes of water-soluble resins of the thermoplastic type have been discussed in appropriate sections earlier in this chapter. For example, methyl cellulose and other soluble cellulose derivatives were described in section 3.2.3. and polyvinyl alcohol was described under Vinyl Resins in section 3.6.4. Methyl cellulose and other soluble cellulose derivatives are typically employed as thickening, stabilizing, and emulsifying agents in water-base paints more often than as coatings in themselves. Polyvinyl alcohol, while used for the above purposes, also finds use as a film in its own right because of its excellent resistance to organic solvents and its high degree of impermeability to vapors and gases. Moreover, although polyvinyl alcohol itself is a linear thermoplastic polymer, it can be crosslinked with suitable chemical agents to insolubilize it, as noted in section 3.6.4.

3.16.2. Thermosetting Types

The success of water-thinned latex paints in the consumer field has led to intensive effort on the part of resin producers and paint manufacturers to develop practical and durable water-base industrial coatings that will combine the safety and convenience of latex paints with the high film integrity of solution-type coatings. Such coatings are based on a water-soluble resin that can be converted by heat, oxidation, and/or chemical agents into a crosslinked, insoluble, thermoset material. A general discussion of water-solution type coatings, indicating background, properties, formulation, and use, was presented in section 2.3.6. A more specific discussion of the resins themselves is given here.

The thermosetting water-soluble resins generally contain hydroxyl and/or carboxyl groups, the latter sometimes reacted with a volatile organic base such as morpholine, to render them water-soluble. These same polar groups impart a chemical reactivity to the polymer molecule which permits it to be crosslinked by reaction with a suitable resin or drying oil, under the influence of heat, oxygen, and/or catalysts. Amino resins have been particularly effective for this purpose.

A water-soluble melamine-acrylic resin for industrial finishes has been described [123] which is available as a clear solution in water, requiring only the addition of pigment to produce a ready-to-spray enamel. When baked, the acrylic and melamine components become crosslinked to form a hard, durable, high gloss finish said to be comparable to the best melamine-alkyds.

Water-soluble baking resins composed of

trimellitic anhydride, a glycol, and a dicarboxylic acid have been described [64]; these are self-curing vehicles which, on baking at 350 to 500 °F (177 to 260 °C), are reported to yield coatings having high gloss, good flexibility and impact resistance, high hardness, good mar resistance, excellent salt-spray resistance, and good resistance to hot detergents. Vehicles in which the trimellitic resin is combined with a water-soluble amino resin can be baked at temperatures as low as 250 °F (121 °C) to yield coatings having high gloss and good mar resistance; such resin blends are somewhat less flexible and less resistant to detergents than the self-cured vehicles.

Technological advances from development work now in progress can be expected to yield an increasing number of water-soluble resins for industrial applications in the not-distant future.

3.17. Miscellaneous Resins

3.17.1. Resin Combinations

The scope of this work has permitted consideration of only the main classes of resins and resin combinations. Obviously, many other combinations are possible through chemical reaction or physical blending, and have yielded a wide variety of materials for specific coatings applications. The essential properties of this at-first-glance bewildering array of materials can often be assessed, for practical purposes, from a knowledge of the properties of the individual constituents, many of which have been discussed in this chaper.

3.17.2. Resins Discussed Elsewhere

In some cases, information concerning the properties and uses of particular materials has been given elsewhere in the text, where this appeared logical and appropriate; for example, *terpene resins* and *coumarone-indene resins*, being primarily varnish resins, were discussed in section 2.2.2 on Varnish and have been omitted from the present chapter. In other cases, information relating to a particular class of resins has been distributed among several places in the text to make it available where it was most appropriate or needed; thus, those aspects of *polyvinyl acetate* and *styrene-butadiene resins* which relate directly to latex paints are discussed in section 2.3.5, while the general properties of these resins are discussed in sections 3.6.1 and 3.7.2 of the present chapter. Similarly, *water-soluble resins* have been discussed at several places in the text (see sections 2.3.6 and 3.16). In such instances, the treatment has been selective rather than repetitious, with appropriate cross-references within the text. The comprehensive Index will provide a ready guide to all the information relating to a particular resin or subject within the scope of this publication.

3.17.3. Natural Resins

These have received only brief treatment herein (sec. 2.2.2). Aside from their diminishing (though still important) use in the coatings field because of their replacement by the more uniform and versatile synthetic resins, natural resins have been adequately discussed elsewhere [65, 66].

3.17.4. Furan Resins

These are black, thermosetting resins made by the polymerization of furfuryl alcohol in the presence of acidic catalysts. Strong acids, both mineral and organic, cause the polymerization to occur with explosive violence. Furan resins are usually supplied as a partially polymerized, neutralized liquid that remains stable on storage, until cured to an insoluble and infusible resin by addition of dilute acid at the time of use. Because of their dark color, the uses of furan resins are primarily functional rather than decorative. The fully cured resins are resistant to acids (except strong oxidizing types), alkalis, corrosive fumes, and solvents, and find use as industrial maintenance coatings, tank and digester linings, anl laboratory bench tops. For the latter and similar applications, the resin may be polymerized *in situ* by applying alternate coats of furfuryl alcohol and dilute mineral acid, thereby building up a jet-black, chemically resistant finish.

3.17.5. Polypropylene

The polypropylene of current importance is a recent member of the new family of stereoregular polymers (see sec. 3.1.4.5) having an isotactic (highly ordered), highly crystalline structure. (The atactic form is not made commercially.) Its exceptional properties resemble, but surpass, those of high-density polyethylene (see sec. 3.13.1). Although thermoplastic, it possesses unusual heat resistance. Its melting range is from 325 to 340 °F (163-171 °C), and it is capable of continuous service at 300 °F (149 °C). It is stronger and harder than high-density polyethylene, and has greater resistance to organic solvents. Resistance to acids, alkalis, and salt solutions is excellent, even at elevated temperatures. Water absorp-

tion is practically nil, and electrical properties are excellent. While likely to find its widest use in molded articles and film, polypropylene can also be applied as a coating in much the same manner as polyethylene. It can be applied to metals by dipping the heated object into the powdered resin (see fluidized resin bed, sec. 5.4.6) and then completing the fusion and flow-out process by heating in an oven at about 482 °F (250 °C). The coating obtained is heat-sealable, clear, tough, chemically resistant, and highly impermeable to many vapors and gases. Wire coatings, applied by extrusion, exhibit excellent electrical and mechanical properties, with high resistance to heat, cracking, and abrasion. Polypropylene can also be extruded onto paper and fabrics to provide a flexible, durable coating, in a variety of colors. Stabilization against sunlight is accomplished, as with polyethylene, by incorporation of carbon black or other suitable opacifying agents. Although still too new to have achieved wide use, polypropylene is among the most promising of the new plastic materials, and is rapidly becoming more available and lower in cost as commercial production is stepped up.

3.17.6. Polycarbonate Resins (Lexan)

This is another of the new and unusual thermoplastic resins that is now commercially available. It is tough, heat-resistant, dimensionally stable with a low water absorption, and has good electrical properties. It is unstable in the presence of alkali. Its softening range is from 420 to 440 °F (216 to 227 °C), and it exhibits excellent thermal stability; it is virtually unaffecetd by an hour of heating at 570°F (299 °C), as might be required during processing. It is self-extinguishing when burned (ASTM D 635). Its transparency imparts excellent colorability. Its chief applications, at present, are for molded articles such as housings for business machines, electrical apparatus, and portable tools; parts for appliances and heating apparatus, heat-resistant lenses and instrument windows, and molded replacements for die-cast metal parts. The resin can also be extruded into heat-sealable sheet or film and as a wire coating. Although polycarbonate resin is still too new to have found much application in the coating field, its combination of desirable properties coupled with its thermoplastic nature may lead to coatings applications in the future.

FIGURE 3.1. *Roberts jet abrader for measuring abrasion resistance as described in Fed. Test Method Std. No. 141a, Test Method 6193.*
(Photo courtesy of Kameras Instruments.)
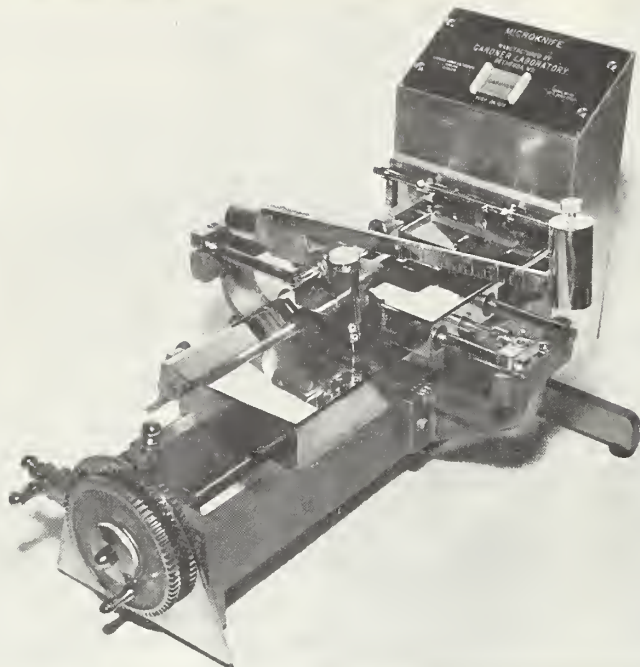
FIGURE 3.2. *Microknife parallel-groove adhesion tester as used in ASTM Method D 2197-67T.*
(Photo courtesy of Gardner Laboratory.)

FIGURE 3.3. *Infrared spectrophotometer is used to identify binders, solvents, and pigments in organic coatings.*

4. Selection of Coating Systems

Selection of the optimum coating system for a given purpose involves the careful consideration of a number of concurrent and sometimes conflicting requirements. The final choice often involves compromises in which moderate shortcomings in secondary properties must be accepted in order to obtain maximum performance with respect to properties of primary importance to the intended application. Sometimes there may be several equally good choices from a performance standpoint; in such situations other factors, such as cost or availability, will govern the selection. Seldom does one find the ideal coating system; that is, one possessing every desired performance property along with low cost, ease of application, and freedom from fire and toxicity hazards.

Despite the basic importance of the cost factor and the universal desirability of safe and easy application properties, all of these are secondary to the actual performance properties of the coating system. Even the cheapest coating material is wastefully expensive if it fails to perform its service function, while an initially expensive material that does the necessary job may prove quite economical in the long run. The old adage about avoiding "penny-wise but pound-foolish" practices definitely applies in the coatings field. Moreover, if the only coating system that will meet the requirements of an essential service application is one that is difficult or hazardous to apply, then the difficulties will have to be met and the risks taken (with all possible precautions) in order to achieve the performance properties without which all else is for naught.

The properties of all important classes of synthetic resins for coatings were discussed in detail in Chapter 3. It now remains for us to consider how this information can best be utilized for the selection of suitable materials for particular applications involving specific types of substrate and service environment.

4.1. Basis for Selection

When one is confronted with the complex problem of selecting the best coating system for a particular application, the basic task is to decide which of the many available resins will best meet the performance requirements. It is at this perplexing and critical point in the planning of an adequate coating system that the responsible engineer, architect, maintenance superintendent, or procurement officer most needs complete, concise, and reliable information to guide his decision, regardless of whether he himself must specify the particular material to be used or whether he must merely choose wisely from among various candidate materials offered by different manufacturers or suppliers.

Although any resin chosen as the film-forming base can be formulated in a great many ways with all sorts of modifications to enhance or diminish certain properties, the fundamental character of the resin continues to be the basic factor in determining the properties achieved. Once the decision as to the basic resin to be employed has been made, the manufacturer can generally be relied upon to supply the best, or at least an adequate, formulation of that type for the particular application. Implicit here is the necessity for the procurement official to inform the coatings manufacturer to the fullest extent possible of the requirements of the application; for only the manufacturer (or his well-informed suppliers) knows just what goes into his own formulation and what its detailed performance capabilities are. It is usually impractical and unnecessary for the procurement official to know or to specify exactly how a given resin is to be formulated, unless a government or other specification is available which spells out such detailed requirements. Very few specifications are so restrictive; many merely stipulate performance requirements, making the burden of proper resin selection and formulation the responsibility of the manufacturer; others specify the basic type of resin (and perhaps certain key modifying ingredients) to be employed, and leave to the manufacturer the task of formulating these basic ingredients into a finished coating material that will meet performance requirements. A convenient guide to organic coating materials covered by Federal Specifications is provided by the guide list and the tabular summary given in chapter 8; however, most of the newer synthetic resin coatings are not yet covered by Federal Specifications.

Application of the information about synthetic resins given in chapter 3 to the problem of coating selection will be greatly facilitated by a logical approach involving:

(1) Consideration of such factors as service environment, nature of substrate, basic function to be provided, appearance desired, application limitations, and cost—leading to

(2) Designation of various factors or properties as being of either primary or secondary importance in the intended application.

(3) Scanning of the information on specific resins given in chapter 3, to select those resins which possess all (or as many as possible) of

the properties of primary importance. Such scanning may be minimized by limiting it to those classes of resins which are indicated in subsequent sections of this chapter to be suitable for use on the specific substrate and in the particular environment of the intended application; it should be recognized, however, that many less commonly used but potentially applicable materials may be found in the greater detail of chapter 3.

(4) Final selection of the most suitable resin (or resin blend, if necessary) on the basis of the number of desirable secondary properties it possesses IN ADDITION TO the primary properties that led to its preliminary selection. The above points will be developed in subsequent discussion.

Where the problem is to determine whether or not a specific type of coating material being offered for a particular application is basically suitable for that application, the above approach provides a ready answer, since it is necessary to refer only to that section of chapter 3 in which the resin in question is discussed.

Where the task is to specify or select the most suitable coating for a particular application, the problem is obviously more diffuse and difficult, since, theoretically, one has the whole field of synthetic resins to choose from. Even here, however, the approach suggested above can provide a solution. Often, to one who has some familiarity with organic coatings, several candidate materials will immediately suggest themselves (see section 4.6 on Functional Coatings). It is then necessary only to check the appropriate sections of chapter 3 against the check-list of desired properties in order to select the most suitable of these materials. If the "most suitable" material thus chosen does not possess all of the required properties, or if it is desired to make certain that a better material has not been overlooked, it will be necessary to study the information in chapter 3 more fully. In such cases, and in situations where a group of potentially suitable materials is not known, the broad field of organic coatings can be narrowed by considering the nature of the substrate, as discussed in subsequent sections 4.2, 4.3, 4.4, and 4.5 of this chapter. These sections indicate classes of materials that are suitable for use, respectively, on wood, metal, masonry, plaster, and wallboard surfaces.

At most, the task of selection will require a careful reading of all of chapter 3 as well as the present chapter. The reader will thus gain a knowledge of the properties of synthetic resins sufficient to enable him to immediately eliminate some materials as unsuitable, while pointing to others as potentially suitable materials from among which a final selection can be made on the basis of a detailed study of their properties in relation to the needs of the application.

With a general approach to the problem of coatings selection now in mind, let us consider in greater detail those factors which constitute a basis for the checklist of primary and secondary properties to be evaluated in conjunction with the information on synthetic resins given in chapter 3.

4.1.1. Service Environment

A detailed consideration of the type of service to be encountered will yield many of the items needed for our checklist of properties. Is the service environment to be an interior or an exterior one? What are the durability or longevity requirements—is maximum longevity desired, or is a temporary coating or a strippable coating needed? What specific endurance properties are needed—resistance to heat, cold, sunlight, general weathering? Is resistance to chemicals required—if so, to which types—solvents, acids, alkalies, detergents, continual water immersion? Will the coating be subjected to alternate soaking and drying, in which case a material of low water absorption and good dimensional stability will be necessary. What mechanical properties are needed—should the coating be hard, flexible, tough, rubbery? Must it be resistant to abrasion, impact, flexing? What are the adhesion requirements? The answers to questions such as the foregoing will help to bring the problem into focus.

4.1.2. Nature of Substrate

While seeking a coating having properties that will enable it to withstand the rigors of the service environment to which it will be exposed, one must also consider the nature of the substrate to be coated. For example, a coating capable of giving excellent service in a particular environment when applied on a metal surface may fail badly in that same environment if applied on wood, partly because of the poorer dimensional stability and greater coating elasticity requirements of wood surfaces. On the other hand, a satisfactory coating for wood may be lacking in adhesion to a nonporous surface such as metal, or it may fail to provide adequate corrosion resistance. Coatings for masonry or plaster must be resistant to the alkalinity in such surfaces, and must give good holdout (uniformity of coverage and appearance) despite the porous and non-uniform nature of such surfaces.

It is evident, therefore, that both the choice of the film-forming resin and its formulation into a suitable coating must take into account the chemical and physical nature and the surface topography of the substrate. Smoothness, porosity, dimensional stability, corrodibility, dampness, alkalinity, hydrophilic or hydro-

phobic character—all of these attributes of the surface to be coated affect the choice of a proper coating system. In many instances, the diverse requirements of substrate and environmental factors necessitate a dual or multiple coating system in which a primer of specific composition is used to satisfy substrate adhesion and corrosion-resistance requirements while a coating of a different composition is used as the topcoat to withstand environmental conditions. Sometimes an intermediate or tie-coat is used between primer and topcoat to improve the bond between them or to provide special properties such as filling, hiding, and bodying.

In general, it may be stated that a coating material for metal surfaces should at least have good wetting properties and good specific adhesion, as well as good film integrity to aid corrosion resistance. Coatings for wood must have, among other properties, good flexibility and elasticity and, in many applications, a moderate degree of permeability to water vapor in order to perform satisfactorily. Coatings for masonry must be water- and alkali-resistant, have good sealing properties, and be permeable to water vapor. Coatings for plaster, in addition to being moisture- and alkali-resistant, must have a controlled degree of penetration to provide both good adhesion and adequate topcoat holdout.

Specific information on coatings for various types of substrates is given in sections 4.1 through 4.5 of this chapter.

4.1.3. Basic Function

In selecting a suitable coating for a particular application, it is helpful to keep in mind the basic function (protective, decorative, or functional) that the coating is to fulfill, for this can aid considerably in the compilation of an appropriate checklist of required properties. If the basic purpose of the coating is to protect a surface from harmful environmental agents (for example, weathering, fumes, or chemicals), it is obvious that specific resistance to these environmental factors is of primary importance while other factors, such as appearance, are secondary. If the coating is to provide mainly a decorative function, the emphasis shifts to factors such as color and gloss, and the retention of these properties in service; here, the character of the pigment (see sec. 2.3.1) and the pigment volume concentration (PVC) of the formulation play an important role along with the resin itself.

In cases where the coating is to fulfill one or more definite functional purposes (see sec. 4.6), certain specific properties can be listed immediately as of primary importance. Thus, a coating for an industrial smokestack must be

heat-resistant and weather-resistant. A coating for a home space heater must be both heat stable and color stable at elevated temperatures. Floor coatings must be tough (hard yet flexible) to withstand the scuffing and abrasion received in service.

Color and surface texture (gloss) are prime factors in determining the heat and light reflectivity or absorptivity of a surface; it is well-known that light colors and glossy surfaces reflect heat and light, while dark surfaces absorb such radiation. For example, an outdoor storage tank exposed to the heat of the sun will be maintained at a considerably lower temperature if a light-colored rather than a dark-colored paint is applied to its surface. Heat build-up in such a tank can also be lessened (though not to the extent achieved with a white paint) by employing a metal-pigmented coating (e.g., an aluminum paint), which possesses a high specular reflectivity. Aluminum-pigmented paints are useful further for their very good weathering properties.

Other examples of functional coatings are low-modulus or soft materials for acoustical applications, rubbery coatings to provide resilence, coatings of high dielectric strength for electrical insulation, high visibility coatings incorporating fluorescent pigments, and coatings with a high degree of imperviousness to vapors and gases for packaging applications.

Some types of functional coatings depend strongly upon certain additives in addition to the film-forming resin to achieve their purpose. For example, despite the importance of the resin in a high-visibility paint, it is the fluorescent material (see sec. 2.3.1.8) that contributes the basic functional property. Similarly, fire-retardant coatings (sec. 2.3.8) depend heavily on special types of pigments, fillers, plasticizers, and flame-retardant additives to achieve their purpose. Anti-static (explosion-proof) floor coatings for hospital operating rooms, in addition to being based on an abrasion-resistant resin, are formulated with sufficient carbon to render them adequately conductive. Fungus-resistant coatings often contain a fungistat or a fungicide as well as a resistant resin. So-called sanitary or hygienic coatings incorporate a bacteriostatic substance to keep the surface "germ-free". Functional coatings such as the foregoing emphasize the importance of the entire formulation as well as the resin itself in producing a suitable coating material for a given application.

4.1.4. Appearance

Coating appearance is a consideration in most coatings applications and becomes a factor of primary importance in cases where the coating serves a decorative function. Aside from

the color itself, the appearance of a coating is determined by its degree of transparency, translucency, or opacity; by its degree of gloss or flatness; and by its surface topography which may be, for example, textured to simulate fabric or leather, wrinkled or hammertoned to provide special effects, or multicolored to give interesting and pleasing color effects while hiding substrate imperfections.

4.1.4.1. CLARITY AND WHITENESS.—With the exception of clear coatings, white coatings, and a few specialized finishes (e.g., wrinkle and multicolor finishes), most of the appearance properties of a coating are determined more by the manner of formulation and application than by the nature of the resin itself. Clear, colorless coatings are required where a natural finish is desired to protect an already attractive surface such as beautiful-grained wood or bright metal. Outstanding clarity and transparency, together with maximum retention of these properties on aging, can be obtained with coatings based on cellulose acetate butyrate and on acrylic resins. However, many other resins which yield clear, colorless films are described in Chapter 3, including cellulose derivatives, various vinyl resins, and polystyrene, and circumstances often dictate the choice of one of these. For example, in an application in which a clear coating is desired which must also withstand a considerable amount of abrasion, a clear vinyl coating might be more suitable, because of its inherently greater toughness, than an acrylic coating of better clarity but lesser abrasion resistance.

White coatings should be based on colorless or nearly colorless resins that do not tend to yellow with age. Excellent retentive white finishes can be made with resins such as melamine- or urea-formaldehydes, vinyls, acrylics, selected alkyds, and various cellulose derivatives. Good white finishes can also be made with resins that have only a pale yellow color, such as epoxies and drying-oil alkyds. Properly formulated polyurethane coatings give good results as clear finishes for boats and exterior wood siding, but they tend to darken somewhat during exterior exposure and hence do not make the best white finishes. Phenolic resins also are transparent enough to yield satisfactory spar varnishes and floor coatings; however, their yellow color, which darkens considerably with age, limits their usefulness as clear coatings and makes them unsuitable for white or pastel finishes. In general, even resins with only a slight yellow or amber cast are unsuitable for applications where maximum clarity and transparency are required, as in coatings for artistic paintings, important documents, silver objects, and optical devices.

4.1.4.2. Some resins normally yield TRANSLUCENT COATINGS. Among these are the fluorocarbon resins, polyamides, and conventional polyethylene (high-density polyethylene is relatively clear). Ordinarily clear coatings can be made translucent by incorporating small quantities of a finely divided extending pigment or filler (see sec. 2.3.1.3), or a somewhat incompatible resin or plasticizer, to produce a colloidal suspension that will scatter the transmitted light.

4.1.4.3. OPACITY is achieved by incorporating hiding pigments into the formulation. The opacity or hiding power increases with increasing pigment volume concentration and increasing index of refraction of the pigment (see sec. 2.3.1.2).

4.1.4.4. A GLOSSY SURFACE is the rule with clear films laid down from solution in a good solvent. Glossy surfaces are the result of good coating flow-out and leveling and good film integrity, resulting in an optically smooth surface. Some resins are inherently capable of yielding films with exceptionally high gloss; notable among these are polyurethanes, alkyds, and epoxy-polyamides. Poor gloss (surface dulling) of unpigmented coatings may result from improper formulation or from poor application techniques or conditions. For example, if the solvent portion of a sprayed coating is too lean in active solvent, or excessively fast in evaporation rate, the deposited film may be too viscous for good flow-out or too dry for good coalescence, so that an optically or visually rough surface is produced. "Blushing" of the film under high humidity conditions, or "blooming" due to migration of an incompatible constituent to the surface or resulting from an undesirable chemical reaction at the surface, also may destroy gloss. More information on the relationships between formulation, application conditions, and film properties is presented in section 5.3.2, and in section 7.2.

The degree of gloss exhibited by a pigmented coating depends primarily on the pigment volume concentration (PVC) and, in general, decreases with increasing pigmentation. Thus, enamels are formulated within a PVC range of 15 to 30 percent, with the highest gloss enamels in the low PVC portion of this range. Gloss paints are usually in the PVC range of 30 to 45 percent. Semi-gloss paints are in the 40 to 55 percent PVC range. Flat paints are formulated with PVC's generally in the 50 to 65 percent range. Above this range, the critical PVC (beyond which the paint properties undergo a pronounced and usually undesirable change) is liable to be exceeded, although the actual critical PVC depends on the nature of the materials (vehicle, pigments, extenders, etc.) involved.

Although pigment volume concentration is the chief factor determining the gloss of pigmented coatings, other factors such as fineness of grind, compatability of vehicle components, vehicle dispersive power, and other formulation variables also affect the degree of gloss obtained. As in the case of clear films, the gloss of pigmented coatings also depends on the manner of application and on the prevailing application conditions, inasmuch as both of these affect the structure of the film laid down.

4.1.4.5. Textured coatings having a wrinkled, crackled, pebbled, hammertoned, or other intentionally "faulty" film structure or finish find use both for their pleasing appearance and their serviceability. Such coatings can provide an attractive and durable finish on physically imperfect surfaces that might require costly surface preparation if coated with conventional smooth finishes. They are based on special resins and formulating ingredients and specially balanced solvent mixtures. The effect achieved also depends importantly on the manner of application. Various kinds of textured coatings are described below:

4.1.4.5.1. *Wrinkle finishes* are formulated for fast drying that will form a surface "skin" and cause partial setting of the film before much flow and leveling occur. Continued rapid curing and escape of solvent sets up shrinkage stresses and strains that cause the film to wrinkle. It is apparent that the film must be flexible if it is to wrinkle rather than crack under the high drying stresses developed. Wrinkle finishes are usually based on an alkyd or varnish vehicle in which the modifying oil is of a very fast drying type, usually tung oil or oiticica oil. Phenolic resin-tung oil combinations have been notably successful in this type of finish. To achieve the necessary fast dry and cure, high proportions (10 to 20 times greater than usual) of efficient driers such as manganese and cobalt are used in the formulation, and a high proportion of low-boiling fast-evaporating solvents is employed. To further develop the wrinkle effect, the coating is generally applied in a single thick coat and is baked to complete the cure. Fine rather than coarse wrinkle finishes can be obtained by applying the above principles in less drastic fashion.

4.1.4.5.2. *Crackles finishes* are obtained by over-coating an ordinary protective base lacquer with an over-pigmented, brittle coating that will crack under the stresses developed during drying. The base coat is usually of a contrasting color to that of the crackle coat. A clear protective topcoat may be applied over the crackle coat if desired.

4.1.4.5.3. *Pebble finishes* are obtained by spraying a high viscosity coating of high solids content and fast setting time onto a smooth base coat in such manner as to produce blobs of coating material that set before flow and leveling can take place. Through control of viscosity, air and fluid pressure, and speed of travel of the spray-gun, the pattern of blobs can be varied to give a variety of textured surfaces, from a uniformly pebbled finish to one resembling leather grain. Pebble finishes can be formulated with high quality resins such as vinyls, epoxies, and alkyds that do not require further protective overcoating. Simulated leather finishes having excellent chemical resistance, abrasion resistance and general durability can be made with vinyl plastisols (see sec. 3.6.2); these must be given a flash bake to fuse the applied coating into a continuous film.

4.1.4.5.4. *Hammertone finishes* are generally one-coat, sprayed coatings formulated with a small amount (1 or 2 ounces per gallon of vehicle) of a fine grade of non-leafing aluminum pigment plus minimal amounts of such other colors as may be desired. The solvent mixture is a combination of fast and slow evaporating solvents that permits the coating to set fast enough to prevent running and sagging while maintaining good fluidity long enough for a vortex action to be set up in the drying and cooling coating. The swirl of aluminum particles in the convection currents leads to the typical hammertone configuration in the set film. After a short period of air-drying, hammertone finishes are baked for final cure. Since hammertone finishes are largely the result of the solvent balance and manner of application of a coating, they may be based on a variety of different resins selected on the basis of the protective and durability requirements to be met.

4.1.4.5.5. *Multicolor finishes* consist essentially of discrete particles of two or more different colored, organic solvent-base materials suspended in an aqueous solution of a water-soluble polymeric stabilizer. A discussion of such finishes is given in section 2.3.7. They are being used with particular success as interior architectural finishes for wood, masonry, plaster, and wallboard—including difficult surfaces such as basement walls and ceilings of hospitals and garages as well as walls and furniture in hotels, industrial plants, public buildings, and homes. Durable types for use on exterior masonry or metal also are available. In addition to their generally good durability and pleasing appearance, multicolor finishes offer easy application with a minimum of surface preparation, good hiding of surface imperfections, uniform masking of areas of different porosity or texture and easy touch-up of damaged areas when necessary.

4.1.5. Application Limitations

In selecting a coating material for a given purpose, it is necessary to take into account such characteristics as toxicity, flammability, odor, drying speed, moisture sensitivity, brushability or sprayability, and other inherent properties that affect the manner of application. For example, toxic or flammable coating materials cannot be used in areas where, for operational or economic reasons, it is not feasible to shut down the operation. Nor should toxic or flammable materials be used without adequate safety equipment and precautions, particularly in confined areas. A desirable coating system that requires several days for application and cure would not pose a problem in a new building not yet occupied; however, in an occupied hospital or in a busy restaurant, an odorless fast-drying coating such as a latex paint might be far more feasible. The ability to dry very quickly is a necessary requisite for traffic paints—one which excludes many otherwise satisfactory materials.

Other examples of application limitations affecting the broad choice of film-forming resin or type of formulation may be given: When painting must be done in cold weather (never desirable but sometimes necessary), a latex paint might be unsatisfactory because of poor coalescence (or even freezing) at low temperatures. Plastisols require a flash fusing to form a continuous film. Heat-convertible coatings cannot be used unless adequate oven or infrared baking facilities are available. Oil paints do not perform well if applied over damp or alkaline surfaces. Latex paints require oil-base primers before application to wood surfaces. Polyurethanes adhere better to water-base stains than to oil-base stains. Phenolic paints (sec. 2.3.2.2) require thorough surface preparation and limited inter-coat drying periods to give good adhesion. Multicolor finishes must be applied by spraying—the high shear involved in brushing would destroy the emulsion and discrete character of the particles of colored lacquer. Two-component coatings, such as air-drying epoxies, which must be activated just before use, require (unless brushing is to be employed) a special type of spray gun that will meter and mix the components at the gun at the instant of spraying. And so on (also see sec. 7.2.4.3).

In short, in choosing a coating material, due consideration should be given to its application properties in relation to available facilities and the environmental conditions under which it will be applied.

4.1.6. Cost

Last but far from least among factors to be considered in the selection of coating systems is the inevitable item of cost. Despite the basic importance of the cost factor, it must always—in any honest appraisal of ultimate economy of coating operations—be weighed against the performance properties and requirements of the coating system. A low-cost coating that fails to perform its function is a completely wasted expense. Considering the relatively high cost of labor involved in applying protective coatings, a short service life of a cheap but inferior material may make ultimate coating and maintenance costs far higher than if a more expensive but more durable coating had been employed in the first place. This is not to say that cheap coatings are necessarily inferior, or that an expensive coating automatically will perform well. Obviously, it depends on the requirements of the application. Where, for example, a relatively inexpensive rosin-modified phenolic will perform satisfactorily in an interior application, it would be a useless extravagance to use the more expensive pure phenolic type. The latter, on the other hand, would be more economical, in the long run, for an exterior application. Similarly, an expensive premium material such as a fluorocarbon resin would be quite inferior as a coating for a masonry wall compared to a much less expensive latex paint.

Aside from the ultimate cost of a coating material in relation to its suitability and durability in a given application, and apart from the intrinsic cost of the film-forming resins and other ingredients that make up the formulation, a number of specific application factors must be taken into account in arriving at an over-all cost estimate. Thus, in addition to the *gallon cost* of the material as purchased, one must also consider the *spreading rate* (i.e., the area adequately covered by a unit volume of coating material, usually expressed as square feet per gallon), the probable *application time* and its equivalent in *labor costs,* the investment in regular or special *equipment required* for application of the material, and finally the expected *useful service life* of the coating.

In the absence of actual experience with a particular material, it is apparent that much of the information needed for a cost estimate must come from the coatings manufacturer. Information on surface preparation, spreading rates, application methods, drying time, type of service for which recommended, and an indication of the order of durability to be expected in the intended application is usually furnished by the manufacturer, and is generally reliable if the manufacturer is a reputable one (also see sec. 7.2.2).

4.2. Coating Systems for Wood

Wood is a porous, hydrophilic material of relatively poor dimensional stability. It swells and shrinks, expands and contracts, with changes in moisture content and temperature. A coating that is to perform successfully on a wood surface must therefore be distensible and elastic enough to follow the dimensional changes in the wood without cracking. Good wetting and controlled penetration of the porous wood surface are also requirements for obtaining good adhesion and adequate holdout of topcoats. On exterior wood surfaces that are subject to absorption and migration of moisture from within, as exterior wood siding on a house, the coating must have the additional property of permeability to water vapor; otherwise, the entrapped moisture is likely to cause blistering and peeling of the paint film. Even so, excessive amounts of moisture originating inside a structure must be controlled to ensure satisfactory paint performance.

A satisfactory coating system for wood generally requires the use of a primer or undercoater to lightly penetrate and seal the wood, followed by one or more topcoats of a coating that will provide the necessary protective properties and desired appearance. For exterior use, the primer is usually a specially formulated oil or oleoresinous type, as described in section 2.4.1 and typified by Federal Specification TT-P-25; however, self-priming (thinning with linseed oil) is sometimes resorted to as a matter of convenience, or when a lead-free coating system resistant to sulfide fumes is required. On interior wood, the first coat is frequently a long oil-alkyd enamel undercoat, such as that described by Federal Specifications TT-E-543 or TT-E-545; alternatively, when convenience dictates, an appropriate topcoat material may be made into a self-primer by thinning with one pint per gallon of a suitable thinner (see sec. 5.3.2). Other federal specifications for wood primers are TT-P-636 and TT-P-659 (see tabular summary in chapter 8).

The above remarks relating to wood primers apply primarily to conventional coating systems for wood in which the topcoat is an oil-base or oleoresinous material. The newer synthetic resin coating systems, based on resins such as cellulose acetate butyrate, polyesters, and many others may require different types of primers, most frequently a thinned (self-primed) version of the topcoat material. The directions furnished by the manufacturer of such coatings are the best guide to the type of primer or sealer required. A discussion of the types of materials suitable as the main body or finish coatings for wood is given in the following sections.

4.2.1. Exterior Coatings for Wood

Linseed oil house paints, properly formulated and pigmented, remain one of the best and most durable coatings for exterior wood structures in ordinary environments. The linseed oil film owes its effectiveness to a unique combination of desirable properties (see sec. 2.3.2.1 on Oil Paints), including good adhesion, elasticity, permeability, and weather resistance. Despite limitations such as relatively poor water-, chemical-, and abrasion resistance, linseed oil paints are excellent in general durability and performance when applied to exterior wood siding on homes and other buildings.

On exterior wood surfaces that are free from the problem of moisture entrapment and the related blistering of the paint film, oleoresinous coatings (see sec. 2.3.2.2) such as oil-modified alkyds or oil-modified phenolic types may be used. Long oil-alkyds make excellent architectural paints for exterior trim and trellis applications. Alkyd paints dry faster and harder than straight oil paints, and have better gloss and color retention along with excellent general durability. Paints based on silicone-modified alkyd and phenolic resin vehicles also are finding use on exterior wood.

Where a clear finish is desired on exterior wood surfaces, phenolic-tung oil spar varnishes (and to a lesser extent, alkyd varnishes) are used. Clear coatings are considerably less durable than pigmented ones (see sec. 2.3.1.1). Where a good oil or oleoresinous paint may give four or five years of satisfactory service, a clear finish based on the same vehicle may fail in a year or two, or even sooner.

Woods exposed to marine or immersion conditions, as on boats and over-water structures, have traditionally been protected with tung oil-phenolic spar varnishes, particularly those based on 100 percent phenolic resins. Not yet fully evaluated, but very promising in these applications, are newer coatings based on epoxy resins, epoxy-polyamide resins, polyesters and polyurethanes.

On new wood surfaces, including exterior wood siding, latex paints based on acrylic or on polyvinyl acetate resin emulsions are proving satisfactory, *provided the wood is first treated with a zinc-free oil-base primer*. With somewhat greater difficulty, latex paints may also be applied over previously painted wood surfaces, if loose chalk is first removed and an oil-base primer applied in accordance with the manufacturer's instructions.

Wood surfaces, such as porches and decks, that are subjected to considerable abrasion and

wear as well as weathering require coatings based on tough, durable vehicles. The most widely used vehicles for this purpose have been medium or long oil alkyd or phenolic varnishes, particularly tung oil-phenolic types. A typical oleoresinous floor and deck enamel is described by Federal Specification TT–E–487. More recently several of the newer synthetic resins, especially epoxies, polyurethanes, and polyesters, are finding increasing use in floor and deck finishes; properly formulated and applied (sec. 5.3.3.) they are capable of excellent service in such applications, although more expensive than oleoresinous types.

Wood furniture that is to be subjected to outdoor exposure can be protected with coatings based on alkyd or phenolic varnish vehicles, cellulose acetate butyrate lacquers, polyester resins, polyurethane finishes, and epoxy resins.

Federal specifications for organic coatings for exterior wood surfaces are limited chiefly to a variety of oil, oleoresinous, and alkyd types. The newer synthetic resins to which reference has been made, while of great potential usefulness in this area, have not yet been described by formal Federal specifications. Existing Federal specifications for exterior wood coatings may be readily located by means of the classified list and summary charts given in chapter 8.

For maximum usefulness, the information given in this and other sections of this chapter on the suitability of various types of coatings for use on a specific substrate in a particular environment should be supplemented by referring to the detailed information about these resins which is given in chapter 3. For example, such reference to the information on phenolic resins will indicate that while modified phenolic resins are used to some extent in exterior finishes (in cheaper finishes, or in small proportions to improve the adhesion of a pure phenolic resin), it is the 100 percent phenolic types which have the best exterior durability.

4.2.2. Interior Coatings for Wood

Interior coatings for wood, in addition to the general requirements for good adhesion and adequate coverage, are usually expected to be relatively quick-drying, reasonably free from obnoxious odors and toxic ingredients, attractive in color and appearance, stain-resistant, washable, and scuff-resistant. Good flexibility is a necessary property, but elasticity requirements are less severe than for exterior coatings. Since resistance to sunlight and weather is not needed, interior coatings may often be formu-

lated with less durable and less expensive resins, pigments, and additives than are required for exterior finishes.

For interior woodwork, cabinets, and furniture, the most thoroughly proven and widely used paints are those based on alkyd resins, particularly medium oil soya-modified types. Several Federal specifications for interior alkyd-base paints are included in the summary given in chapter 8.

For the clear finishes generally desired on furniture, oleoresinous varnishes (see sec. 2.2.2) and cellulosic lacquers are widely used. Most of the latter are based on cellulose nitrate modified with suitable resins and plasticizers. Cellulose acetate butyrate lacquers also are useful in this application. Polyester coatings, though rather difficult to apply, are finding increasing use as premium furniture finishes of great beauty and durability. Epoxy resins and polyurethanes may be used as furniture coatings; their toughness and durability, however, have led to their wider use as clear finishes for wood surfaces (e.g., gymnasium floors) that must withstand severe abrasion and wear.

Clear coatings for interior wood paneling may be based on the same resins indicated above for furniture finishes. Bleached shellac varnish [151] is often used as an attractive, non-darkening finish for wood paneling, although it is more brittle and less durable and chemical-resistant than many other materials. The shellac may be used as a sealer for the wood, and then over-coated with a more durable and resistant finish such as an oleoresinous varnish.

Shellac is used also as a floor sealer, with a protective overcoat of hard wax. A durable floor sealer based on a tung oil-phenolic varnish resin is described by Federal Specification TT–S–176. Floor sealers are designed to penetrate and seal the wood, leaving only a thin film on the surface which does not show wear as readily as thicker varnish coatings. Durable polymeric floor finishes are available based on a variety of resins or blends of resins such as maleic-modified alkyds, resin-modified phenolics, cellulose derivatives, and natural resins. A conventional floor and trim varnish is covered by Federal Specification TT–V–71. For maximum durability with minimum maintenance in severe service applications such as bowling alleys, gymnasium floors, and areas of heavy foot traffic, polymeric coatings based on polyurethane or epoxy-polyamide resins are proving highly useful. Where resilience and oil and chemical resistance are paramount factors, neoprene coatings may be used on floors.

A coating for laboratory bench tops, with

excellent resistance to acids, alkalis, and other corrosive chemicals, can be built up with furan resins (see sec. 3.17).

Most of the resins mentioned above in connection with clear coatings may serve also as the basis for pigmented paint vehicles.

4.3. Coating Systems for Metals

Although metals are impermeable to moisture and gases and are relatively stable dimensionally, the common structural metals—particularly iron and steel—are very susceptible to corrosion in a moist atmospheric environment (above 60 per cent relative humidity at ordinary temperatures), particularly under acidic conditions such as occur in industrial atmospheres. Corrosion is an electrochemical process in which chemical changes are produced in the metal by the flow of current caused by differences in electrical potential arising between dissimilar metals or between dissimilar areas in or around the same metal. The flow of current dissolves away the anodic (corrodible) material while affording protection to the cathodic material. Moisture on the metal surface provides a conductive path through which corrosion currents can flow. The presence of soluble salts or other electrolytes on the metal surface greatly accelerates the corrosion process and may lead to severe localized corrosion in the form of pitting. Oxygen or oxygenated areas are in effect cathodic toward iron and steel, so that rusting (oxidation) takes place rapidly in the presence of oxygen and moisture. The rust formed is permeable to moisture and is strongly cathodic to the underlying iron or steel, so the corrosion proceeds until the metal is destroyed. Mill scale also is cathodic to iron and steel, and is usually cracked or loosely bonded; hence the need to remove it, if possible, before painting, especially if the steel will often be wet or immersed during service (see secs. 6.3.1 and 7.2.3).

The corrosion of metal which is in continuous contact with a conducting medium such as moist soil or water can be suppressed by imposing an electric current sufficient to render the metal completely cathodic. Such *cathodic protection* is particularly applicable to the exterior of buried pipelines, the interior of water tanks, and the exterior of ship hulls. In general, however, the most practical and by far the most widely used method of protecting metal against corrosion is by the proper application of a suitable organic protective coating system that will prevent moisture and oxygen from reaching the surface of the metal and will act as a barrier against galvanic current (see sec. 7.2.3). All elements of such a system—surface preparation and pretreatment, primer, intermediate and finish coats—must be selected with the type of service in mind, and with care to ensure that all parts of the system are compatible (see sec. 7.2.2.3). Compatibility implies that each part of the system will bond properly to other parts and to the substrate in such manner as to achieve a composite system that will remain intact and perform its protective function for the maximum possible time.

The information to be presented represents established good practice in the selection of coating systems for metals, particularly steel. Adherence to the suggested practice will ensure a compatible coating system capable of excellent service in the intended application. In cases where it is not possible to follow the optimum procedures indicated, deviations are permissible provided precautions are taken to avoid possible difficulties. For example, although it is ordinarily not good practice to apply a phenolic topcoat over an oil-base primer because of the danger of lifting the undercoat, this may be done successfully if the oil-base primer is allowed to dry thoroughly before application of the topcoat. More information of this kind is presented in section 7.2.2.3.

A satisfactory coating system for metal begins with the application of a suitable corrosion-inhibiting primer to the clean (and often chemically pretreated) surface. The primer, ideally, should have good wetting properties (see sec. 7.2.4.1) to provide adequate adhesion to the nonporous metal surface and to ensure penetration into crevices and into areas of rust or scale difficult to completely remove (as on structural steel). It should also, of course, provide a strong bond with the topcoat. So long as the primer remains intact, excellent protection against corrosion is afforded the substrate. An important function of the topcoat (body or finish coats), therefore, is to protect the primer against wear and deterioration so that it can continue to perform its corrosion-inhibiting function. Additionally, the topcoat should have a high degree of imperviousness to moisture, give the desired appearance, and possess adequate over-all durability in the environment in which it is to serve.

The primary purpose of this section, as with others in this chapter, is to provide information on the *selection* of coating systems, by indicating classes of resins or coatings which are particularly well-suited for use on a given surface under various specified conditions. Important adjunct information is given at appropriate places elsewhere in the text, as follows: The

formulation and selection of primers for ferrous metals, galvanized surfaces, aluminum, and magnesium are discussed in section 2.4.2. Corrosion-inhibiting primers derive their special protective qualities from the corrosion-inhibiting pigments which they contain; these pigments and the manner in which they function are described in section 2.3.1.5. Information on the surface preparation and pretreatment of metals is covered in section 6.3. In general, once the metal has been adequately prepared and the proper corrosion-inhibiting primer applied, the topcoat materials that may be used are similar for most metals. The selection of topcoat materials possessing the good film integrity and other attributes necessary for good performance on metals is discussed below. Oil-base, alkyd, phenolic, and vinyl types are widely used. Also useful for particular applications on metal surfaces are coatings based on epoxy resins, polyamides, epoxy-polyamides, chlorinated rubber, neoprene, polysulfides, polyesters, polyurethanes, cellulose esters, styrene-butadiene copolymers, and other synthetic resins; these often require special primers which should be applied in accordance with the instructions of the manufacturer.

4.3.1. Coatings for Structural Steel

The everpresent need for protecting from corrosion the vast quantities of structural steel in use has led to the development of effective protective coating systems for these materials. Chief among such systems from the standpoint of wide use are the time-tested oil-base and oleoresinous (alkyd and phenolic) types. Of proven usefulness among newer types of coating materials are systems based on vinyl resins; these have been particularly effective under severe corrosive conditions, such as immersion in sea water or exposure to industrial and chemical environments. Also proving useful under conditions of continual water immersion and severe marine service are the new zinc rich paints (see sec. 2.3.1.5) based on high percentages of zinc dust in epoxy, epoxy-polyamide, polyurethane, and other alkali-resistant vehicles [128]. Where high resistance to strong acids and alkalis is required, excellent protection is afforded by chlorinated rubber coatings. Chlorinated rubber is also an excellent primer for metal that is to receive neoprene coatings in applications requiring exceptional resistance to abrasion, such as structures exposed to wind-driven sand. The choice of an optimum coating system that will provide adequate protection at minimum cost requires consideration especially of the condition of the surface to be painted and the nature of the exposure environment.

4.3.1.1. OIL-BASE AND OLEORESINOUS SYSTEMS. —A common problem in the painting of structural steel surfaces is the presence of harmful rust and mill scale impractical to remove completely. Such steel requires a linseed oil-base primer to provide adequate wetting and penetration of pores and crevices. The primer must also contain corrosion-inhibiting pigments to passivate the steel surface. A typical excellent primer for this purpose is the straight red-lead-base linseed oil paint covered by Federal Specification TT–P–86, Type I. Where faster drying is necessary and some sacrifice in wetting ability can be tolerated, the type II material of the above specification may be used instead of type I. The type II primer is based on a red lead-iron oxide-extender mixed pigment in an alkyd varnish-raw linseed oil vehicle that will air dry in about 16 hours as compared to about 36 hours for the straight oil base (type I) material.

On smooth, thoroughly clean steel, quick-drying corrosion-inhibiting primers based on poorer-wetting but more durable alkyd or phenolic varnish vehicles may be used. A typical red lead-alkyd varnish (linseed oil-modified) primer that dries in about 6 hours is described by TT–P–86, Type III. The straight alkyd varnish vehicle possesses better water and chemical resistance than the straight oil base (type I) and oil-fortified alkyd varnish (type II) vehicles, but it should not be used as a primer on incompletely cleaned steel because of its limited wetting properties.

Very good durability under conditions of fresh-water immersion, high humidity and condensation, or moderately severe chemical atmospheres is obtained with corrosion-inhibiting primers based on a straight phenolic-tung oil varnish vehicle such as that typified by TT–P–86, Type IV. The latter contains a red lead-plus-extender mixed pigment. While having excellent durability under adverse conditions, its limited wetting ability restricts its use to thoroughly clean steel, preferably steel that has been blast cleaned or pickled.

An alternative to the red lead type primers discussed above are primers utilizing a zinc yellow-iron oxide mixed pigment as the corrosion-inhibiting base in an oleoresinous vehicle. The three types described by Federal Specification TT–P–57 are typical; the pigment portion contains some zinc oxide and a substantial proportion of siliceous extenders in addition to the main pigments. The vehicle for type I is a 50/50 blend of a long oil-alkyd resin with raw linseed oil; its slow drying and good wetting properties permits its use on steel limited to wire-brush cleaning. Type II is based on a medium oil length alkyd vehicle; although faster drying and more durable than type I, its poorer

wetting properties permit it to be used only on smooth, thoroughly cleaned steel; it is intended for use as a factory or industrial primer rather than for structural steel. Type III is based on a straight phenolic-tung oil vehicle that provides good durability under conditions of severe humidity or fresh water immersion; however, its limited wetting properties restrict its use to thoroughly cleaned steel (sandblasted or pickled), preferably steel that has received a phosphate pretreatment.

A corrosion-inhibiting primer based on the unique basic lead silico chromate pigment described in section 2.3.1.5 is available under Federal Specification TT–P–615, in four types that are similar in application to the four types of red lead-base paint described in TT–P–86 and referred to above. The type I vehicle is a 4:1 blend of raw linseed oil with a long-oil alkyd resin; it provides good wetting of metal despite the presence of small amounts of corrosion products impractical to remove. The type II vehicle is a 1:1 blend of raw linseed oil with a medium-oil alkyd resin; although its wetting properties are not as good as that of type I, it may be used where faster drying is necessary. The type III vehicle is an alkyd varnish that may be used only on thoroughly clean steel because of its fast drying and low wetting properties. Type IV is based on a phenolic-tung oil vehicle that provides good durability under severe humid conditions or fresh water immersion; however, its fast drying and limited wetting ability restricts its use to steel that has been thoroughly cleaned, preferably by sandblast. The basic lead silico chromate pigment may also be incorporated, in combination with conventional pigments and extenders, into a variety of vehicles to produce intermediate coat and finish coat paints with corrosion-inhibiting properties.

For the protection of potable water tanks, a zinc dust pigmented primer and paint based on a phenolic varnish vehicle is very suitable. Such a paint [152] is covered by Military Specification MIL–P–15145 (Formula No. 102).

4.3.1.1.1. *Intermediate and finish coats.*— Intermediate coats for application over the primers that have been discussed may be the same as the primer coat or the same as the finish coat material to be used. Finish coats should be selected with system compatibility kept in mind. Thus, as a general rule, oil-base primers should be over-coated with oil-base topcoats, alkyd primers with alkyd topcoats, and phenolic primers with phenolic topcoats. Variations from the rule are permissible if special precautions are taken to ensure compatibility and intercoat adhesion, as discussed in section

7.2.2.3. A variety of oil-base and oleoresinous intermediate and finish coat paints and enamels, in many different colors, are covered by Federal specifications. The classified list given in chapter 8 will provide a ready guide to the letter-number designations of these specifications; composition and performance information for most of them can be found in the tabular summary of that same chapter.

Among finish coat materials suitable for use, over the aforementioned primers, on structural steel and other exterior metal surfaces, the following are typical: A linseed oil paint incorporating a titanium-lead-zinc type pigmentation, is covered by Federal Specification TT–P–102; it is available in white and light tints and has good resistance to weathering in ordinary environments. A lead-free, fume-resistant linseed oil paint (white only) is described in TT–P–103. Black linseed oil paints with very good durability are covered by TT–P–27 and TT–P–61. A durable red iron oxide paint (so-called "roof and barn paint") based on a varnish-fortified linseed oil vehicle is specified in TT–P–31. A chrome-green long oil-alkyd paint (known as a "trim enamel paint") is covered by TT–P–71. Where the greater resistance of an alkyd resin is needed in a coating for relatively smooth steel that has received an oleoresinous primer, an alkyd gloss enamel such as that described by TT–E–489 offers excellent durability in ordinary atmosphere; a semigloss alkyd enamel is covered by TT–E–529, and a lustreless alkyd enamel by TT–E–527. For severe service under conditions of continuous condensation or fresh water immersion, in conjunction with phenolic varnish-base primers, a highly durable (weather- and water-resistant) aluminum phenolic paint can be prepared by adding two pounds of aluminum pigment paste (TT–P–320, Type II, Class B) to one gallon of phenolic resin spar varnish conforming to Federal Specification TT–V–119; however, aluminum-pigmented vehicles are not suitable for use in strongly alkaline or acidic environments. There, inert pigments are required.

4.3.1.2. VINYL SYSTEMS.—For the protection of structural (and other) steel exposed to severely corrosive conditions in industrial or marine atmospheres, chemical environments, condensation, and alternate or continuous immersion in fresh or salt water, coating systems based on vinyl resins give excellent service. For optimum results the steel should be cleaned by blast or pickling to remove rust, mill scale, and all traces of oil or grease. The clean surface must be pretreated with a vinyl washcoat or wash primer such as that specified in Military Specification MIL–C–15328 (Navy Stand-

ard Formula No. 117) before application of the regular vinyl primer. The wash primer provides a mild phosphating action in addition to depositing a thin vinyl film that provides an anchor for the corrosion-inhibiting primer which follows. The most widely used vinyl priming paint for steel is a red lead type [143, 145] such as that conforming to MIL–P–15929 (Formula No. 119). A zinc chromate vinyl priming paint [144] such as that conforming to MIL–P–15930 (Formula No. 120) may also be used with good results.

The intermediate coat may be the same as the priming coat or the same as the finish coat. The most durable and chemical-resistant finish coats are based on straight vinyl resins, typically a vinyl chloride-acetate copolymer resin, together with inert pigments. Aluminum-pigmented vinyl paint will give excellent service in marine atmospheres or fresh water immersion but should not be used in strongly alkaline or acidic environments. Straight vinyl resin paints incorporating suitable inert pigments are resistant to direct liquid contact with severely corrosive chemicals such as inorganic acids, alkalis, and salts; they are resistant also to aliphatic liquids, oils, greases, and alcohols; however, they are attacked by strong oxidizing acids and by many aromatic organic solvents (see sec. 3.6.3).

Where the maximum durability and chemical resistance of straight vinyl paints is not required, excellent service under severe exposure conditions (as on the boot-topping areas or on the topsides of marine vessels) may be obtained with vinyl-alkyd paints such as those described in a series of Military specifications comprising the Standard Formula 122 series [68]. These are a series of paints ranging in shade from black through gray to white, in either gloss or dull finish. Their numerical designations include the following: MIL–P–15932 thru 15936, –16188, –16501, –16502, –16738 [55].

4.3.1.3. BITUMINOUS COATINGS (also see sec. 2.5) may be used on iron and steel subjected to severe corrosive atmospheres or underground burial. For best results the steel should be blast cleaned or pickled. For very severe exposure a wash primer pretreatment is helpful before application of cold-applied asphalt or coal tar mastics. Coal tar mastic must be over-coated with coal tar emulsion to prevent checking and cracking on exposure to sunlight. For underground use in very corrosive soil, best results are obtained with a coal tar primer topcoated with coal tar enamel (wash primer is not suit-

able in coal tar enamel systems). In noncorrosive soil, an asphalt varnish such as that covered by Federal Specification TT–V–51 may suffice. All bituminous coatings are resistant to water immersion, but not all are suitable for potable water. (For the latter application, coal tar enamel has been widely used.) Although bituminous coatings are resistant to many chemicals, they are attacked by many organic solvents and by some chemicals and must be used with discretion. For example, the coal tars have good resistance to aliphatic liquids but poor resistance to acids, while the reverse is true for the asphalts.

4.3.1.4. GALVANIZED STEEL may often be painted without undue difficulty if the galvanized surface is well-weathered but free of dirt and rust. However, new galvanized steel must be solvent-cleaned to remove all oil and grease and for best results (if not factory chromated) should be pretreated with a basic zinc chromate washcoat or cold phosphate pretreatment (see sec. 6.3.3.1). A zinc dust primer such as that covered by Federal Specification TT–P–641 adheres well and provides good protection for galvanized surfaces; it will also perform well as the finish coat except in acidic environments. The TT–P–641 zinc dust paint is available in three types: Type I, based on a raw linseed oil vehicle, provides the best wetting but is slow to dry. Type II, the type most often used, is based on a long oil, linseed-modified, alkyd resin vehicle that has moderately good wetting properties and is faster drying than the straight oil type. Type III is based on a pure phenolic resin spar varnish vehicle that is suitable for use under severe moisture conditions or underwater exposure; however, its limited wetting properties require that the steel be thoroughly cleaned and given a phosphate pretreatment before application of the primer. In the case of the type I and type II materials, pretreatment, while beneficial, is optional.

Badly rusted galvanized steel should be cleaned like ordinary rusted steel before painting is attempted. Where it is not possible to remove all corrosion products, a wetting oil (thinned linseed oil) pretreatment may be used to ensure a bond between the primer and the steel. The wetting oil treatment permits use of the faster drying primers (types II and III) which cannot ordinarily be used on incompletely cleaned surfaces.

4.3.2. Industrial Coatings for Steel

Factory-coated steel products such as railroad cars, vehicles, machinery, tools, garden equipment, appliances, metal furniture, etc., may be protected or decorated with a wide variety of organic coatings. The opportunity afforded in the factory for thorough surface preparation and pretreatment, coupled with selection of a primer and finish coat system suited to the service environment, leads to excellent service performance. Most factory-applied coating systems utilize quick-drying, baking-type primers and finish coats. Baking makes possible a rapid production line coating operation and results in the development of maximum adhesion and optimum film properties.

For general use in ordinary environments, both interior and exterior, medium- to short-oil alkyd resin vehicles of the baking type are most widely used. Where exceptional whiteness and color retention together with very good mar resistance are required, as on refrigerators, washing machines, hospital equipment, etc., non-drying oil alkyds modified with urea- or melamine-formaldehyde resins give excellent service. A detailed discussion of the applications for which the various types of alkyd resins are well-suited is given in sections 3.4.1 and 3.4.2.

Baked phenolic resin coatings, particularly those based on pure phenolic resins of the alcohol-soluble, thermosetting type (see sec. 3.3.2.3), are highly resistant to corrosive atmospheres, organic solvents, and organic and mineral acids (except strong oxidizing types); they have proved durable also when submerged in water or buried in soil.

Excellent chemical and abrasion resistance is achieved with baked epoxy resins (see sec. 3.10). Many of the properties of the baked resin are retained in the amine-catalyzed types which cure at room temperature. Zinc-rich paints (see sec. 2.3.1.5) based on epoxy-type vehicles are giving good service as corrosion-resistant coatings for the undersides of automobiles.

Vinyl coatings, especially vinyl chloride-acetate copolymer types, are widely used for the protection and decoration of metal, in both smooth and textured finishes (see sec. 3.6.3, and the discussion of textured finishes in sec. 4.1.4.5). Plastisols based on polyvinyl chloride resins (sec. 3.6.2) yield tough, chemical- and abrasion-resistant coatings for severe service applications such as plating baths, dish-washer racks, and chemical tanks.

Lacquers based on cellulose nitrate, cellulose acetate butyrate, or acrylic resins are often used for the protection or decoration of metal. General purpose nitrocellulose lacquers are described in Federal Specifications TT-L-26 and TT-L-31. The latter is suitable for exterior use on smooth clean metal—for refinishing or as the original finish—on vehicles, construction equipment, metal signs, railing, etc.

Other industrial coatings for steel include those based on polyamide and epoxy-polyamide resins, polyurethanes, polyesters, and neoprene. Coating systems suitable for steel fuel tanks and salt water tanks are described [142] in Mil. Spec. MIL-P-23236.

All the coating systems which have been discussed require proper cleaning and in some instances pretreatment of the metal surface, as well as suitable primers to provide corrosion-inhibition and topcoat adhesion. The instructions furnished by the manufacturer usually provide the best guide to their application.

4.3.3. Coatings for Other Metals

Coatings for aluminum, magnesium, brass, copper, and other metals are, in general, similar once the metal has been properly cleaned, pretreated, and primed. Pretreatments and primers for aluminum and magnesium and their alloys were discussed in sections 2.4.2.3 and 2.4.2.4. Additional detailed information on various metals is presented in section 6.3 of chapter 6 on Surface Preparation and Pretreatment. Copper (section 6.3.6.3), after being cleaned and perhaps roughened slightly or pretreated, may be primed with an aluminum varnish such as TT-V-81 or with a zinc dust priming paint such as TT-P-641. Thinned, carbon-pigmented oil paints such as TT-P-61 also may be used as a primer on copper. Terneplate (sec. 6.3.6.6), or "roofing tin," may be painted with ordinary iron oxide-pigmented paint such as TT-P-31; new terne plate must be wiped free of all oil or grease, using solvents such as turpentine or gasoline; the paint should be well brushed out, since thick coats are prone to crack later.

When coatings based on synthetic resins (epoxies, polyurethanes, polyesters, neoprenes, etc.) are selected, the manufacturer's instructions with respect to choice of primer and manner of application should be closely followed to achieve optimum results.

The list of finish coat materials that may be used over suitably primed metal is a long one that includes many of the synthetic resins discussed in detail in chapter 3. Mention has already been made, in connection with the discussion of coatings for steel, of oil-base and oleoresinous coatings, vinyls, epoxies, polyamides, polyurethanes, polyesters, neoprene, chlorinated rubber, cellulose esters, and other film-forming resins. The reader is referred to the information given in section 4.1 of this chapter for guidance in a systematic basis for utilizing the comprehensive information on synthetic resins presented in chapter 3.

4.4. Coatings for Concrete and Masonry

The chief characteristics of concrete and masonry surfaces that must be considered in the formulation and selection of satisfactory coating systems are their porous, often rough texture and the alkaline nature of the portland cement contained in concrete, stucco, asbestos-cement shingle, and in the mortar used in brick* and cinder block construction. Superimposed on the inherent porosity of these materials is a surface topography which may vary from the relative smoothness of cast concrete to the gross irregularity of stucco. An additional characteristic that must be considered is the hydrophilic nature of concrete and masonry surfaces, as well as the fact that wherever portland cement is present, some of the water originally used to prepare it may be present in both hydrated and adsorbed form.

A coating that is to perform satisfactorily on concrete and masonry surfaces must therefore be sufficiently free-flowing to follow and coat the macroscopic roughness of the surface and yet not penentrate deeply into the pores; otherwise, the pores would soak up so much paint that good hold-out of topcoats would be difficult and costly to obtain. Additionally, the coating should be insensitive to the moisture and alkalinity likely to be present in such substrates, particularly those which are unaged.

Before applying paints to concrete and masonry, the surface must be properly cleaned and, preferably, in the case of open-textured surfaces such as cinder block, filled with a suitable grout coat. Surface preparation is discussed in section 6.4. A primer or primer-sealer is applied to the prepared surface before application of finish coats, except when cement-water paints or whitewash are used. The primer is often simply a thinned version of the finish paint. A detailed discussion of primers for concrete and masonry is given in section 2.4.3.

Coating systems for concrete and masonry may be a cement-water type, an oleoresinous type, a latex-base (water-thinned) type, or a synthetic resin type. These are discussed below (for whitewash, see sec. 2.3.9.2).

4.4.1. Cement-Water Paints

Cement-water paints, the oldest type, are composed chiefly of portland cement with some lime (see sec. 2.3.9.1), and are low in cost. When properly applied and damp-cured, they can provide a very durable finish that is perme-able to moisture but unaffected by dampness or alkalinity. They may therefore be used above grade outside, and either above or below grade inside, on aged or unaged concrete and masonry surfaces. Cement-water paints have good hiding and decorative qualities but become somewhat translucent and darker in color when wetted. Upon drying, the original opacity and color are regained, but there may be a period of mottled shading while the drying is taking place. Cement-water paints will not adhere well to previously painted or chalky surfaces and will be weak, brittle, and prone to cracking if not kept damp during cure, especially during the first 48 hours after application.

4.4.2. Oleoresinous Paints

Oleoresinous paints, while attractive in appearance, are capable of satisfactory performance only when applied on dry, well-aged (3 to 12 months) concrete or masonry. Their limited resistance and permeability to moisture does not permit their use below grade or in other applications where moisture behind the film can cause it to blister and flake. A suitable oleoresinous paint for application to thoroughly aged, dry, exterior concrete surfaces is described by Federal Specification TT–P–24; an aluminum-pigmented paint based on TT–V–81 mixing varnish also may be used. Oleoresinous paints suitable as both primer and finish coat on aged, dry, *interior* concrete and masonry surfaces are covered by Federal Specifications TT–P–30 and TT–P–47 as well to TT–P–24. Alternatively, for interior masonry, if the surface is sealed with an oil-base primer-sealer, such as that described by Federal Specification TT–P–56, and given a suitable enamel undercoat (such as TT–E–543), then almost any conventional oleoresinous interior paint may be applied as the finish coat. (Additional information on oleoresinous paints is given in sec. 2.3.2.2.)

4.4.3. Latex Paints

Latex paints, because of their good durability and relative insensitivity to dampness and alkalinity along with ease of application and clean-up, have become the most widely used coatings for both exterior and interior concrete and masonry surfaces. (A comprehensive discussion of latex paints is given in sec. 2.3.5.) All three main types of latex paint—acrylic, polyvinyl acetate, and styrene-butadiene—may be used on either exterior or interior concrete or masonry; however, best results on exterior exposure are obtained with the acrylic and the

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* Painted brick surfaces can be durable only if the brick itself endures. In new construction, the proper grade of brick for the environment should be specified independently of subsequent painting considerations. For exterior use, grade SW or MW as defined in ASTM Standard C 62–62 T should be used [160].

polyvinyl acetate types, while the unmodified styrene-butadiene type is generally restricted to interior use. The finish coat material, when thinned, may serve also as the primer-sealer. As with other masonry paints, it is important that the surface be adequately prepared (clean, chalk-free, and filled if necessary) before paint is applied. Since the paint itself is water-based, dampness of the surface is not a problem. The good resistance of latex paints to alkalinity permits them to be used on unaged (but not on fresh, uncured) concrete and masonry. Federal Specifications for exterior latex paints include TT–P–19 (acrylic), TT–P–55 (polyvinyl acetate), and TT–P–99 (styrene-butadiene). An interior latex paint of unspecified resin type is covered by TT–P–29.

4.4.4. Synthetic Resin Coatings

Synthetic resin coatings, other than latex paints, which are being used successfully for severe service on concrete and masonry include epoxy resins, polyesters, polyurethanes, and various synthetic rubbers. Filled epoxy resins and filled or glass-fibre reinforced polyester resins can be applied in thick mastic-like coats to yield hard, glossy, tile-like coatings having great mechanical strength, high chemical resistance, and great beauty. Polyurethane resins produce tough, durable coatings for concrete floors; they are also used in swimming pool paints because of their good water and alkali resistance. Of proven durability and widest use among swimming pool paints are those based on a chlorinated rubber vehicle; such a paint is covered by Federal Specification TT–P–95. Solution-type styrene-butadiene coatings also

are used for this purpose. A synthetic rubber-base paint for interior concrete floors exposed to dampness is described by TT–P–91. Also useful for chemical- and abrasion-resistant service on concrete and masonry are coatings based on synthetic rubbers such as neoprene, chlorosulfonated polyethylene, and polysulfides.

Traffic paints for concrete (and bituminous) surfaces on streets, highways, and airfields are formulated with a variety of quick-drying resins and solvents, including short-oil alkyd and phenolic varnishes, styrenated-alkyds, chlorinated rubber, and solution-type styrene-butadiene resins, together with suitable pigments and plasticizers to produce a tough, adherent, weather-resistant coating. Federal Specifications for traffic paints include TT–P–85, TT–P–87, and TT–P–115.

Multicolor coatings (see sec. 2.3.7) can provide an attractive and durable finish for concrete and masonry surfaces. They may be formulated for either interior or exterior use. A multicolor lacquer based on an alkyd-modified cellulose nitrate vehicle is covered by Federal Specification TT–L–45; type I is for interior use and type II for exterior.

The suggested uses for the various synthetic resins indicated above are not mutually exclusive; many of the resins may be used with good results for applications for which others have been mentioned as outstanding. Reference should be made to the detailed information given for each resin in chapter 3 and to the guidelines given in section 4.1 of this chapter to provide a sound basis for the selection of an optimum coating material for the intended application.

4.5. Coatings for Plaster and Wallboard

The key to successful painting of plaster and wallboard is in the selection and proper application of a suitable primer-sealer (see sec. 2.4.4). Primer-sealers are specially formulated materials designed to properly seal the porous surface, bond well to the topcoat, and provide good topcoat hold-out. They are available either as oleoresinous or latex-base types. The oleoresinous types offer the good brushability, leveling, and adhesion typical of oil-base paints, and provide better wetting and adhesion on chalky surfaces than is obtained with the latex types. They should be applied only on dry, well-aged (60 to 90 days) plaster. The latex-base primer-sealers are characterized by ease of application, fast drying, and good water and alkali resistance. The latter permits their use, if necessary, even on damp or only briefly aged (but not freshly applied) plaster, provided topcoating is deferred until the primed plaster has dried ade-

quately. Whenever possible, new plaster should be allowed to dry for at least two weeks before applying even a primer-sealer. Latex-base primer-sealers, such as that covered by Federal Specification TT–P–650, are particularly well-suited for application on gypsum wallboard ("sheet rock") because of their nonsensitivity to the alkalinity in the plastered tape joints employed and because they do not raise the nap of the outer paper layer as do oleoresinous types. A phenolic emulsion-type dry wall primer also is available for use on gypsum wallboard.

Composition-board (fiberboard) and other non-alkaline wallboards (see sec. 6.5.2) may be sealed with either the latex or oleoresinous type of primer-sealer with good results. (Primer-sealers are also discussed in sec. 2.4.4.)

Either the latex-base or oleoresinous type of primer-sealer may be over-coated with virtually

any conventional type of finish coat—latex, oil-base, or alkyd. A latex paint suitable for interior use both as primer-sealer and finish coat is described by Federal Specification TT–P–29; "self-priming" is accomplished by thinning with water. An oleoresinous primer-sealer is provided by TT–P–56, and an alkyd flat paint suitable for use both as primer-sealer and finish coat is covered by TT–P–30. A wide variety of oil-base and alkyd-base coatings suitable for application on properly primed plaster and wallboard are covered by Federal specifications and may be readily identified through the quick guide list and the tabular summary presented in chapter 8.

In a three-coat oleoresinous system, the middle coat may be an enamel undercoater such as that conforming to Federal Specification TT–E–543 or TT–E–545 (odorless). A one-coat oleoresinous finish is provided by TT–P–47; however, such a coating should not be expected to provide the appearance and durability obtainable with multiple-coat systems.

Multicolor finishes (see sec. 2.3.7) may be applied on plaster and wallboard with attractive results. They are particularly effective in masking surface imperfections and obliterating differences between dissimilar substrates. A multicolor lacquer based on an alkyd-modified cellulose nitrate vehicle is covered by Federal Specification TT–L–45.

In short, in coating plaster and wallboard, apply the right primer-sealer to the properly aged and prepared substrate, and almost any conventional type of finish coat may be applied over it without difficulty.

4.6. Functional Coatings

The preceding sections of this chapter have dealt with the problem of selection of coating systems chiefly from the standpoint of the type of substrate involved and whether the service environment was an exterior or interior one. In general, this is a practical and effective approach to the problem of coatings selection. There are times, however, when the importance of one or more functional properties overshadows ordinary environmental and substrate considerations—when the problem of selection can best be narrowed by first examining those materials which are capable of providing one or more all-important functional properties. This is particularly true when the functional requirement is a very rigorous one. For example, if complete inertness to all known chemicals at temperatures up to 500 °F (260 °C) is required, then the quest for a suitable material can at once be narrowed to polytetrafluoroethylene —provided that one knows that this material possesses such resistance.

As part of the philosophy and systematic approach to the problem of coatings selection offered in section 4.1 of this chapter, it was suggested that when the requirements of the application are considered by one who has some familiarity with organic coatings, several candidate materials will often immediately suggest themselves, thus providing a practical starting point for a detailed check of properties among a limited group of materials. For those who may not yet have this familiarity, the information which follows should provide a useful step toward acquiring it. Our treatment of this aspect of coatings selection is not exhaustive and is desirably limited to indicating only those materials which are generally recognized as outstanding with respect to the particular property under consideration. In this way, subjective considerations are minimized and excessive overlapping of candidate materials is avoided.

In making use of the information given, one should guard against the temptation to "over-select"; that is, against choosing a premium material where an ordinary coating would suffice. Over-selection unnecessarily restricts the number of potentially suitable materials, thereby lessening the opportunity for obtaining a coating that meets the minor as well as the major requirements of the application. The fact that a particular resin appears repeatedly in the functional listings characterizes it as a material of exceptionally good all-round properties but does not necessarily make it the best material for every job or even for most jobs. Often, those materials which are outstanding in a number of important functional properties may have disadvantages in other respects, such as high cost, difficult application properties, limited pot life, the need for baking or fusing, etc. An objective appraisal of the properties needed for a given application, along the lines suggested in section 4.1, is essential to ensure a satisfactory coating system at minimum cost.

The ability to associate certain properties with certain materials can be very helpful in narrowing and solving the problem of coatings selection. The following discussion seeks to provide this facility with respect to a selected group of functional properties.

4.6.1. Chemical Resistance

While some organic coating materials may appropriately be called chemical-resistant because of their relative inertness to a wide spectrum of corrosive agents, the term "chemical-resistant" is more meaningful and useful when the types of chemicals to which the coating is

resistant are specified. For example, baked (thermoset) phenolic resin coatings are generally considered to have excellent chemical resistance, and they do—to most acids, fats, oils, organic solvents, and water—but they may be quickly destroyed by strong oxidizing acids or strong alkalis. Generally good chemical resistance may be the rule for a particular material; yet the exception can be costly and dangerous.

The only organic material that is completely inert to attack by all known chemicals (except molten alkali metals, and fluorine at high pressures) is polytetrafluoroethylene. All others, however resistant, have an "Achilles heel" of which the potential user should be aware—by conducting his own tests if necessary. Limitations of knowledge and space preclude a pinpointing of all such weaknesses here. However, the considerable information offered will simplify and expedite the task of coatings selection.

4.6.1.1. ACID RESISTANCE.—Excellent resistance to dilute and concentrated acids (except strong oxidizing types) is provided by coatings of neoprene, polyvinyl chloride, polyvinylidene chloride-vinyl chloride copolymer, polypropylene, polyethylene, and butadiene-acrylonitrile copolymer (nitrile rubber). Excellent resistance even to strong oxidizing acids is provided by polytetrafluoroethylene, polychlorotrifluoroethylene, chlorosulfonated polyethylene [141], isobutylene-isoprene copolymer (butyl rubber), and chlorinated rubber [140]. Good resistance to non-oxidizing acids is also afforded by polystyrene, furan resins, solution-type styrene-butadiene copolymers, silicones, cyclized rubber, polyesters, and acrylic resins; also, by baked thermoset coatings of pure phenolic resins, unmodified epoxy resins, and amino resins.

4.6.1.2. ALKALI RESISTANCE.—Excellent resistance to dilute and concentrated alkalis is provided by coatings of polytetrafluoroethylene, polychlorotrifluoroethylene, polyethylene, polypropylene, neoprene, baked epoxies (unmodified), polyamides, butyl rubber (isobutylene-isoprene copolylmer), polyvinyl formal, polyvinyl chloride, vinyl chloride-vinylidene chloride copolymer, and chlorinated rubber. Good resistance to alkalis is also afforded by polystyrene, furan resins, amino resins, ethyl cellulose, chlorosulfonated polyethylene, styrene-butadiene resins, butadiene-acrylonitrile copolymer (nitrile rubber), polyurethanes, acrylic resins, cyclized rubber, and coumarone resins.

4.6.1.3. OXIDATION RESISTANCE.—In addition to the materials listed as resistant to strong oxidizing acids (sec. 4.6.1.1), good resistance

to oxidation under conditions of exposure to sunlight and weathering is obtained with silicone resins, polysulfied rubber, cellulose acetate butyrate, acrylic resins, polyurethane rubber, polyacrylic ester rubber, polyvinyl acetate, selected alkyds (e.g., melamine- or silicone-alkyds), vinyl chloride-acetate resins (stabilized), epoxy resins, cyclized rubber, furan resins, pure phenolic resins, polyesters, and polyurethanes.

4.6.1.4. RESISTANCE TO ORGANIC SOLVENTS.—Complete resistance to all known organic solvents is provided by polytetrafluoroethylene. Excellent resistance to a wide spectrum of organic solvents is obtained with water-soluble resins such as polyvinyl alcohol and methyl cellulose. Polyethylene is highly resistant to all organic solvents except hot aromatic and chlorinated hydrocarbons. Polypropylene is even more resistant than polyethylene. Excellent resistance to most organic solvents is provided by baked pure phenolic resins, baked epoxies, and furan resins. Polychlorotrifluoroethylene is insoluble in all organic solvents at room temperature but is swelled by halogenated solvents, toluene, diethyl ether, and ethyl acetate; at elevated temperatures it is swelled by still other materials and will dissolve in a few of them. Very good resistance to a wide variety of organic solvents can be obtained with polysulfide resins. Good resistance to many organic solvents is also obtainable with properly formulated polyurethanes, polyesters, vinylidene chloride copolymers with vinyl chloride or acrylonitrile, and epoxy-polyamide resins.

Excellent resistance to aliphatic hydrocarbons, fats, oils, greases, and waxes is obtainable with a wide variety of coating resins, notably the fluorocarbons, polyethylene and polypropylene, neoprene and chlorosulfonated polyethylene, polyvinyl formal and polyvinyl alcohol, cellulose esters, acrylic resins, and most thermoset resins such as epoxies, melamines, polyurethanes, polyesters, etc.

The wide variations in solvent resistance that may result from differences in resin composition and formulation, together with the wide variety of organic solvents that are available, make it necessary to interpret and use data on solvent resistance with discretion backed up by laboratory testing as may be required. It is evident, nevertheless, that the guidelines provided above can minimize the work required by permitting a judicious preliminary selection of potentially suitable materials.

4.6.1.5. WATER RESISTANCE.—Outstanding resistance to water and very low water absorption with excellent dimensional stability are provided by the fluorocarbon resins, polyethylene and polypropylene, polyvinylidene chloride copolymers (saran), polystyrene, chlorinated rub-

ber, and certain silicone resins. Good resistance to water is also provided by cellulose nitrate, cellulose acetate-butyrate, ethyl cellulose, phenolic resins, vinyl chloride and vinyl chloride-acetate resins, acrylic resins, epoxies and polyamides, polyurethanes, and polyesters.

4.6.2. Heat Resistance

The need for heat resistance immediately brings to mind polytetrafluoroethylene, silicone resins, and polycarbonate resin as the outstanding heat-stable resins. Very good heat resistance compared to most resins is provided by coatings of neoprene, polychlorotrifluoroethylene, baked phenolic resins, chlorosulfonated polyethylene, polyvinyl formal, cellulose acetate, ethyl cellulose, isobutylene-isoprene copolymer (butyl rubber), polypropylene, amino resins, furan resins, polyurethanes, epoxies, and styrene-butadiene resins. Polymers with low softening temperatures but good resistance to discoloration or degradation by heat within their working range include acrylic resins, cellulose acetate butyrate, and polystyrene.

4.6.3. Abrasion and Mar Resistance

To be resistant to abrasion a coating material must either be tough and resilient enough to "ride with the punch," or else hard enough to be immune to the destructive stresses to which it is subjected. The resilient type of abrasion resistance is provided by many of the synthetic rubbers (see sec. 3.15), notably neoprene, chlorosulfonated polyethylene, and polyurethane rubber. Outstanding toughness and abrasion resistance also is exhibited by polyvinyl formal and by polytetrafluoroethylene. Hard coatings with excellent mar resistance include baked epoxy resins, amino resins (especially melamines), polyurethanes, baked phenolic resins, and polycarbonate resin. Tough abrasion-resistant coatings are also obtained with polyvinyl chloride plastisols, polypropylene, polyethylene, polychlorotrifluoroethylene, epoxy-polyamides, ethyl cellulose, and various vinyl and styrene-butadiene resins.

4.6.4. Electrical Properties

Excellent electrical properties, including high dielectric strength and arc resistance and low dissipation factor are exhibited by polytetrafluoroethylene, polyethylene, polypropylene, polystyrene, polyvinyl formal, and polyvinyl chloride. Also very useful for electrical applications are neoprene, polychlorotrifluoroethylene, silicone resins, epoxy resins, polyamides, ethyl cellulose, isobutylene-isoprene rubber (butyl rubber), polysulfide rubber, and polycarbonate resin.

4.6.5. Impermeability

Outstanding impermeability to gases and vapors is exhibited by vinyl chloride-vinylidene chloride copolymers, polytetrafluoroethylene, isobutylene-isoprene copolymer (butyl rubber), polyvinyl alcohol, polypropylene, chlorinated rubber, polyethylene, polysulfide rubber, and polyacrylic ester rubber.

4.6.6. Transparency

Outstanding clarity, transparency, and nonyellowing properties are exhibited by acrylic resins, polystyrene, cellulose acetate butyrate, polyvinyl butyral, polyesters, and polycarbonate resin.

4.6.7. Fire Resistance

Among nonflammable resins with self-extinguishing properties are the fluorocarbons, chlorinated rubber, polycarbonate resin, polyvinyl chloride, polyvinyl chloride-acetate, and certain silicone resins.

4.6.8. Radiation Resistance

A definitive statement on the high energy radiation resistance of organic coating materials is difficult because of the limited, often empirical, and sometimes contradictory nature of the available experimental and performance data. Moreover, most of the information concerning organic coatings must be extrapolated or inferred from data obtained on much thicker sheet or bulk plastics. To the extent that oxygen (and perhaps other environmental agents) may affect the behavior of the material under irradiation, such extrapolation may be misleading because the thickness of the material, together with its permeability, determines the quantity of oxygen that can diffuse into it and be available for reaction where radiation effects are being induced below the surface. Thus, a thin film (i.e., a coating) of an oxygen-sensitive polymer—even a relatively impermeable one—may be quickly destroyed by irradiation because of diffusion of oxygen throughout the material whereas a thick sheet or block of the same material may suffer only surface degradation. Nevertheless, a few basic facts about the effects of high energy radiation on polymeric materials can be stated here, and certain polymers may be broadly classified on the basis of their resistance to such radiation. For detailed information, the reader is referred to the literature [155, 156].

It is known that high-energy ionizing radiation (x-ray, γ-ray, β-particles, etc.) induces either crosslinking, chain scission, chain stripping (removal of chain substituents), or a

combination of these processes in high polymeric materials into which the radiation is absorbed. These effects occur regardless of the source of the high energy radiation—whether generated by high voltage electrical machines such as a Van de Graaff generator or a linear accelerator, or emanating from radioactive isotopes such as cobalt-60 obtained by exposing the metal to pile radiation in a nuclear reactor, or from the atomic pile itself. Nor are the effects significantly different whether the high energy radiation is electromagnetic (γ-rays) in nature or in the form of high speed electrons (β-particles). Crosslinking, as explained in section 3.1.1, is a basically favorable process which may improve many of the physical and chemical properties of the polymer, such as imparting greater hardness, better solvent resistance, and a higher softening point. Eventually, however, under prolonged irradiation even the most resistant polymers finally embrittle and deteriorate. Chain scission or stripping, since it degrades the polymer, is detrimental from the start. Whether a given polymer is improved or degraded by moderate doses of high energy radiation depends on whether the cross-linking or the scission (and/or stripping) reaction predominates, as determined by the chemical structure of the polymer; that is, by the nature and bond strengths of the main chain and side groups, steric factors, and the shielding effect of substituent groups. For example, it has been found that pendant benzene rings, perhaps because of their efficient dissipation of energy, exert a shielding effect that protects the main chain from scission and promotes crosslinking rather than degradation. Such is the case in polystyrene which exhibits the greatest resistance to high energy radiation of any of the common plastics. On the other hand, polyvinyl chloride is quickly degraded even by low doses of high energy radiation because of its high susceptibility to chain stripping.

The radiation resistance of high polymers is of interest both from the point of view of obtaining improved (crosslinked) materials through manmade irradiation and from the standpoint of the use of polymeric materials in environments where they must withstand exposure to moderate amounts of radiation, as in a space capsule or satellite. From both points of view, crosslinking rather than chain scission is the desirable effect. Polymers that tend primarily to crosslink under high energy radiation and may therefore be classed as relatively radiation-resistant include polystyrene, polyethylene, polypropylene, linear polyamides (nylon resins), polyesters, and silicones (particularly phenyl substituted types). Polymers that may be considered as moderately resistant to radiation include styrene-acrylonitrile and styrene-butadiene-acrylonitrile copolymers, polyacrylic acid and esters, polyacrylamide, polyurethanes, diallyl phthalates, polychloroprene (neoprene), chlorosulfonated polyethylene, and SBR rubber (formerly called GR–S). Natural rubber, too, can be vulcanized (crosslinked) with high energy radiation. In the case of all the polymers named above, it should be remembered that in the presence of unlimited amounts of oxygen the crosslinking reaction may be offset or even outweighed by increased chain scission.

Finally, it may be helpful to point out those classes of polymers that are known to undergo chain scission and/or chain stripping rather than crosslinking when exposed to high energy radiation and that consequently soon deteriorate under irradiation. Such "negative" information may be particularly useful when applied to polymers that are noted for their outstanding chemical inertness and might therefore have been expected to be radiation-resistant also. The fluorocarbon resins, including polytetrafluoroethylene, polychlorotrifluoroethylene, and polyvinyl fluoride, all are degraded by high energy radiation, especially in the presence of oxygen. Polymethyl methacrylate and cellulose acetate butyrate, though noted for their excellent resistance to weathering and ultraviolet radiation, suffer severe degradation when exposed to high energy radiation. Similarly, polyisobutylene, despite its chemical inertness, undergoes rapid chain scission under high energy irradiation, even in the absence of oxygen. Other common polymers that have shown [157] poor resistance to high energy radiation include polyvinyl chloride homopolymer and copolymers, polyvinylidene chloride, styrene-butadiene copolymer, polyethylene terephthalate, polycarbonate resin, cellulose esters and ethers, and amino resins and phenolic resins unless mineral filled. Mineral filled epoxy resins also have withstood high energy radiation fairly well. It is apparent that reinforcement with inorganic fillers may permit the use of some polymers under radiation conditions that would quickly destroy the unmodified polymer. It is possible also that even the less radiation-resistant materials may be suitable in certain applications where the degradation suffered is not critical (for example, when irradiation results in the loss of elongation or tensile strength in an application where neither property is important because the material needs only to remain in place without physical strain).

4.7. Summary

Briefly, this chapter has indicated both a philosophy and a systematic approach to the problem of coatings selection, together with specific recommendations regarding coating systems for various substrates and environments. The guidelines provided, in combination with the detailed information on the properties of coating materials presented in chapter 3, should furnish a sound basis for the selection of a suitable material for a given application in the great majority of cases. As an added feature, to provide the potential user with a facility for associating certain resins with certain functional properties, section 4.6 has presented a listing of typical coating properties and the resins which are outstanding in providing these properties.
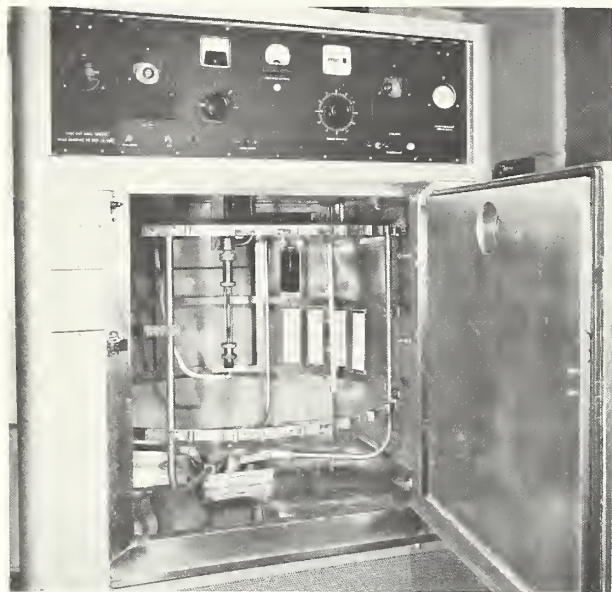
FIGURE 4.1. *Xenon-arc accelerated weathering machine.*
Operating conditions are described in ASTM Method E 240-64T.
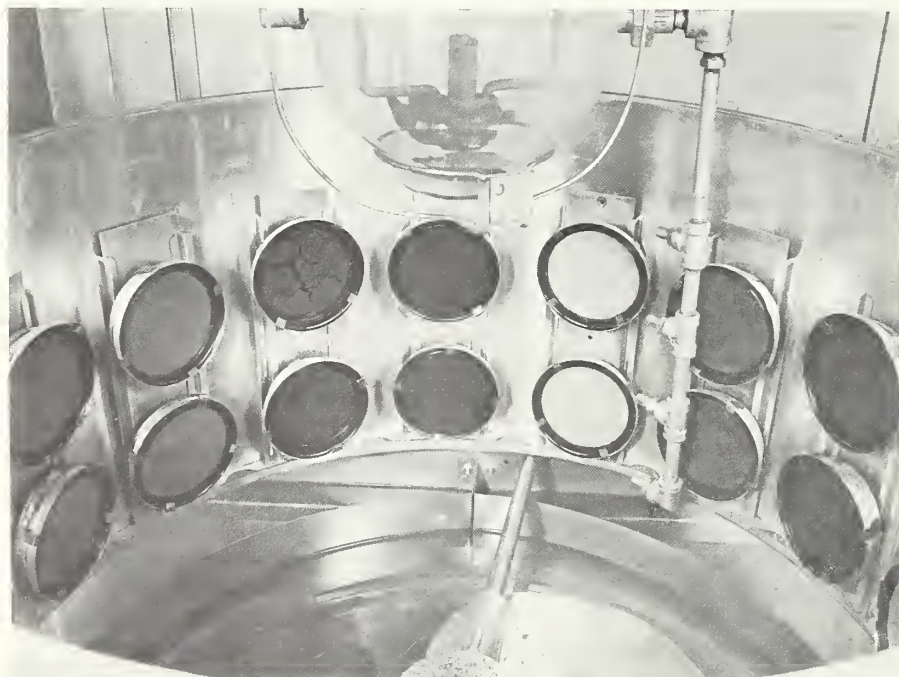
FIGURE 4.2. *Interior of carbon-arc accelerated weathing machine.*
Principles and operating conditions are given in ASTM Method E 188-63T.

5. Storage, Safety, and Application Methods

The proper storage and handling of organic coating materials and the usual methods for applying them are adequately discussed in a number of Departmental and Bureau paint manuals (see references [40] and [41], and General Bibliography in chapter 9). It is not a purpose of this publication to duplicate these detailed treatments of the subject. It is desirable, however, within the comprehensive yet concise scope sought in this volume, to point out the basic precautions that should always be observed in dealing with potentially flammable, toxic, and sometimes "perishable" materials such as paints and other organic coatings. It is also appropriate to present sufficient information about the various methods of applying coatings—particularly the less commonly used or newer methods such as fluidized bed and airless spray—to enable the reader to understand the principle of operation and the chief advantages and disadvantages of each method.

5.1. Storage of Coating Materials

While different coating materials vary greatly in their storage stability—some remaining useable for years while others deteriorate in a few months—all organic coating materials should be stored in tightly closed containers in a covered, well-ventilated area where they will not be exposed to excessive heat, fumes, sparks, flame, or direct sunlight. Heat accelerates the thickening or hardening of reactive vehicles during storage and increases the fire hazard normally present with coating materials containing volatile, flammable solvents. Freezing may break the emulsion and destroy the usefulness of latex paints, although some may withstand a few freeze-thaw cycles; water-base coatings should be protected against freezing. Low temperatures down to 0 °F (−18 °C) thicken but do not ordinarily harm solvent-base coatings; however, the material must be warmed before use to restore a normal viscosity for proper application.

Pigmented materials tend to settle in the container and may form a cake that is difficult to redisperse. Red lead paints are notably troublesome in this respect. Such difficulties can be minimized by inverting containers at intervals of a month or two.

Maintenance of proper identification of paints in storage will save time and avoid costly mistakes. Containers should be relabeled when necessary to ensure legibility. Previously opened containers, in particular, should be checked for tight closure and legibility of identification.

Paint solvents and thinners should be stored with the same or greater care than the paints themselves.

Application equipment should be cleaned promptly and thoroughly with a suitable solvent after each use, and stored in a clean place. Brushes that receive daily use may be kept in good condition by suspending them in a suitable solvent between periods of use; however, this practice may create a fire hazard when volatile solvents are employed unless care is taken to keep the containers well-covered with foil or film or stored in a special cabinet.

5.2. Safety Precautions

The combustible and toxic nature of most organic solvent-base coating materials should be kept in mind whenever such materials are stored, handled, or applied. Containers should be opened carefully in a direction away from oneself or others, since volatiles or unexpected gaseous reaction products may sometimes build up pressure inside the container. Open flames should be kept away from the area where the paint is being used, and sparks should be avoided. Adequate ventilation should be provided indoors to prevent the build-up of toxic or explosive concentrations of solvent vapors. Special precautions are necessary when spraying, whether indoors or outside, to avoid inhalation of toxic fumes and dusts.

5.2.1. Toxicity

Because of its importance to the health of the worker and to those responsible for his safety, the subject of toxicity is discussed here in somewhat greater detail than is found in most paint manuals; however, the treatment is necessarily limited. Detailed authoritative information on the toxicity of specific solvents, pigments, resins, and other constituents of organic coatings is available from the U. S. Public Health Service (Department of Health, Education, and Welfare, Washington, D.C.), in the Chemical Safety Data Sheets issued by the Manufacturing Chemists Association (Washington, D.C.), and in a number of comprehensive reference works [69, 70], Government and industrial pamphlets [71, 72], and manufacturers' technical bulletins.

Even common solvents that are ordinarily considered innocuous may be harmful if inhaled in high concentrations or for prolonged periods. For example, turpentine can cause narcotic poisoning and kidney damage when excessive amounts are inhaled. Systemic damage may

also result from an acute dose (sufficient to produce unconsciousness), or from repeated excessive inhalation of such common solvents as the acetate esters (methyl-, ethyl-, butyl-, and amyl acetate), amyl alcohol, methyl isobutyl ketone, and possibly methyl ethyl ketone. Solvents such as toluene, xylene, ethyl, ether, cyclohexanone, butyl alcohol, and the nitroparaffins have a relatively low chronic toxicity, but their narcotic effect in high concentrations can lead to unconsciousness followed by respiratory failure and death unless the victim is promptly restored to fresh air. Even the least toxic of the common paint and lacquer solvents—including mineral spirits, petroleum naphtha, gasoline, acetone, isopropyl alcohol, and ethyl alcohol—although well-tolerated in relatively large concentrations and having little or no chronic ill effects, can be dangerous in very high concentrations because of their narcotic effect, excepting the alcohols which are irritants (to the eyes and upper respiratory tract) rather than toxicants.

Some common solvents—usually not used directly in paints but often encountered in paint removers and cleaning liquids—are dangerously toxic even at relatively low concentrations; for example, methyl alcohol when inhaled or ingested repeatedly or to the point of unconsciousness may cause death or permanent blindness. Benzene is a dangerous, cumulative poison that causes severe damage to the liver and blood-forming tissues of the body. Many chlorinated solvents, particularly chlorinated aliphatic hydrocarbons, are toxic; chloroform, for example, has poisonous aftereffects, while carbon tetrachloride and now-seldom-used tetrachloroethane are dangerously toxic with severe chronic, cumulative effects on the kidneys, liver, and lungs. Since solvent-type paint removers frequently contain highly toxic solvents, they should be used only with adequate ventilation or a respirator.

The toxic systemic effects of organic solvents can be produced by absorption through the skin as well as by inhalation. Acute or chronic dermatitis or systemic poisoning may result from repeated or prolonged contact of toxic solvents with the skin. Sometimes, the vehicle resin itself may be irritating or toxic to the skin while the resin is in the uncured state. The catalysts or hardening agents (e.g., organic amines) used in two-component coating systems are frequently volatile and toxic materials until they have been incorporated into the resin.

Some of the pigments used in organic coating materials are toxic. Lead compounds and chromates are particularly dangerous, whether ingested or inhaled. Lead fumes generated while burning off old paint are very poisonous. Inhalation of the dust and debris from sanding and brushing operations is a health hazard.

Sandblasting, in particular, requires a suitable mask, goggles, and protective clothing. Some paint additives, such as the mercurial compounds used to impart fungicidal properties, may be toxic if ingested.

The toxicity hazards associated with organic coating materials have been pointed out not to discourage their use or arouse fear but to emphasize the importance of adequate safety measures to prevent accident and injury. With adequate precautions based on knowledge of the properties of these materials, they may be handled confidently and safely. The basic precautions to be observed are simple and practical:

(1) *Avoid unnecessary or prolonged inhalation of fumes and dusts;* always provide adequate ventilation, or use a suitable mask or respirator (remember that gas mask canisters will absorb only limited amounts of noxious vapor and must be renewed at frequent intervals).

(2) *Avoid unnecessary or prolonged contact with the skin;* the use of protective clothing and skin creams will eliminate the need for scrubbing the skin with toxic solvents.

(3) *Avoid ingestion of toxic materials;* wash hands carefully before eating or smoking; change clothing that has soaked up toxic materials.

(4) *Know the material with which you are working;* read and heed the precautions on the label—it will tell you when an unusual hazard exists and how to avoid it.

(5) *Make safety "second nature";* don't sneer at safety regulations or at the fellow who observes them; be alert to possible hazards, avoid them, and stay healthy.

Water-base paints are free from the toxicity hazards associated with organic solvents and are generally based on non-toxic resins. They may contain pigments or additives, however, which may be harmful, so that ingestion should be avoided. The manufacturer's label is a useful guide in such matters.

5.2.2. Fire

Most organic coating materials are combustible (water-base coatings excepted), primarily because of the flammable solvents and thinners which they contain. They are safe while stored in tightly closed containers away from heat and flame. When containers are opened and while the coating is being applied, open flames and heated objects (lighted cigarettes, for example) should be kept out of the area.

When applying organic-solvent base coatings indoors, adequate ventilation should be provided to prevent the build-up of explosive concentrations of vapor. Nevertheless, flame and spark should be avoided. Smoking should

be prohibited. Blow-torches should not be used even in other parts of the building into which solvent vapors may diffuse. Care should be taken to extinguish all pilot flames on heaters and stoves. Sparking motors should not be in operation. Even an electric light switch or the spark from a metal tool can be a source of danger if explosive concentrations of vapor are present—hence the need for adequate ventilation.

Rags used to wipe up linseed oil or other drying oils or oxidizable liquids are a frequent source of spontaneous combustion when left lying around. They should be disposed of by controlled burning, or by drenching them with water and putting them in a covered metal container.

When burning old paint off wood, the torch must be handled with care to avoid setting fire to the substrate. A water hose should be kept ready for use if needed.

Paint and solvent fires usually cannot be fought with water. Water is immiscible with most paint materials; where large quantities of flammable liquids are involved the water will only further spread the flame because the lighter liquids float on the water surface. Such fires are most effectively fought with carbon dioxide, with foam, or with dry-chemical extinguishers, which smother them. This should be remembered if there is ever occasion to use a hand fire extinguisher on burning solvents while waiting for the fire department to arrive. It should be remembered also that fire in a paint storage area may be quickly

followed by explosion as containers become over-heated, and that many burning paints and solvents give off toxic fumes. Chlorinated hydrocarbons, for example, while usually non-flammable or less flammable than most other solvents, give off deadly fumes when heated to decomposition. While it may be worthwhile to fight a small incipient fire with a hand extinguisher while awaiting the fire department, it should be realized that a small fire can develop into a very large fire in a few seconds, with consequent risk to life.

5.2.3. Falls and Spillage

A large proportion of the injuries suffered by painters is the result of falls from ladders or scaffolds, frequently involving paint spillage as an accompanying hazard. Such accidents are usually the result of carelessness in the rigging, maintenance, or inspection of scaffolds and accessory equipment, or in the placement of ladders. Even a short fall can be painful and dangerous. One should be certain that ladders, scaffolds, ropes, and moorings are in proper condition, and that mooring hooks are firmly attached at a location amply strong enough to support the weight. Although these precautions appear self-evident, accidents continue to occur because they are ignored or overlooked.

In the event of a major spillage of volatile flammable liquid, don't wait for a fire—call your disaster control unit or the fire department *immediately*.

5.3. Mixing, Thinning, and Activation

Most of the coatings in use today are ready-mixed materials—ready for use as supplied by the manufacturer except for the need for: (1) stirring or mixing pigmented materials to uniformly redisperse the solids in the vehicle, (2) appropriate thinning when necessary for priming purposes or spray or other application, and (3) proper activation in the case of two-component reactive systems.

In a few instances, the pigment and vehicle of a pigmented coating system are furnished in separate containers for mixing just prior to use in order to avoid undesirable settling, caking, flocculation, or deteriorative changes during storage. For example, aluminum paints [73] are sometimes prepared by mixing the aluminum paste or powder into the appropriate vehicle just before the paint is applied. This procedure is designed to overcome loss of leafing properties of the aluminum pigment and gassing in the container during storage; both of these undesirable characteristics have been encountered with improperly formulated aluminum paints. Gassing (hydrogen formation) may result in the blowing off of friction

top lids from cans with the creation of a fire hazard. Zinc dust paints also are supplied with pigment and vehicle in separate packages because of the tendency toward gassing when mixed with the vehicle and stored.

Before mixing or thinning paint for use, it should be brought, if necessary, to the proper application temperature. Cold paint is most conveniently and safely warmed by letting it stand in a warm room. Where more rapid heating is required, a hot water bath or electric blanket may be employed, but the warming jacket should not be above 90 °F (32 °C). Organic coating materials should never be heated over an open flame because of the great danger of localized overheating, decomposition, explosion, and fire.

5.3.1. Mixing of Paints

Ready-mixed paints are usually furnished in cans of five gallons or less, to permit convenient mixing and to avoid the deterioration that may occur in large containers or drums which are used up more slowly and acquire a large

air space as the contents dwindle. Thorough mixing of pigmented coating materials just before use is necessary to redisperse settled or caked pigment and ensure a smooth, uniform mixture that incorporates all the original pigment into the vehicle. Hand-mixing methods, power stirring, or automatic shaking or vibration may be employed.

Automatic shaking, where available, is convenient and rapid; usually, from three to fifteen minutes is required. The violent agitation, however, produces many fine bubbles in the paint which may be objectionable, particularly in enamels. It may be necessary to let the paint stand for some time to let the bubbles escape and then give it a final mixing by hand before using it. Final hand-mixing is desirable in any event to ascertain that no undispersed material remains on the bottom or sides of the container.

Ready-mixed paint in the usual size containers (up to five gallons) may be hand-mixed conveniently and effectively in the following manner: Pour off the thin supernatant material into a clean container; if only light settling has occurred, pour off about one-third to one-half of the paint. Stir the remaining portion with a paddle or power stirrer until a uniform consistency is obtained, making sure that all material settled on the bottom or sides of the container is re-incorporated. If necessary, stir the poured-off portion also. Slowly, with continual stirring, return the poured-off portion to the original container. Finally, "box" the paint by pouring it back and forth between the two containers several times. While the paint is being used, it should be stirred at frequent intervals to maintain a uniform mixture and to prevent skinning.

When a previously opened container is used again, the same mixing procedure indicated above is used, after first carefully removing any skin that may have formed. If pieces of the skinned material fall into the paint, or if a few small clumps of hard-to-disperse material are present in the paint, these can be removed by straining through clean cheesecloth or fine wire screen. Paint containing a large number of such clumps, or a considerable quantity of settled, caked material that cannot be redispersed, is not suitable for use and should be discarded.

When tinting is to be done, the base paint should be thoroughly mixed before adding the tinting liquid. The latter should be added slowly with continual stirring, and the mixing should be continued until a completely uniform distribution of the tinting color is obtained.

Clear coatings, such as varnishes or clear lacquers, do not ordinarily require stirring. However, if the material near the bottom of the can is thicker than the rest, it should be stirred gently to restore a uniform mixture. Vigorous stirring, particularly shaking, should be avoided, since it introduces air bubbles that will impair the appearance and serviceability of the deposited film. If air bubbles are inadvertently introduced, the coating material should be allowed to stand before use until the bubbles have escaped.

5.3.2. Use of Thinners

The most common reason for thinning paints and other organic coating materials is to reduce the viscosity—either for the purpose of rendering the material suitable for use as a priming coat, or to render it suitable for application by a means different from that for which it was initially formulated. For example, oil-base paints are usually suitable for brush application as furnished; however, they may be thinned further (self-primed) for use as the first coat on bare wood—or they may be thinned to permit their application by spraying. Lacquers, on the other hand, are generally furnished in a viscosity ready for spray application, since this is the preferred method of application. Brushing lacquers also are available—but they must be applied with awareness of their quick-setting characteristics which limit their brushability to only three or four strokes immediately after application.

Quick-drying coating materials such as lacquers, which undergo considerable cooling due to the rapid evaporation of solvent from the applied film, may require the addition of some blush-retardant thinner when applied under adverse conditions of high humidity. "Blush" is a whitish discoloration of the film caused by the condensing of moisture from the air into the drying, cooling film. The visual appearance is the result of: (1) the presence of fine droplets of water incompatible with the organic solvents in the coating, and (2) the actual precipitation, in very fine form, of some of the film-forming material by the nonsolvent water. Although the deposited water will eventually evaporate, the precipitated film material will remain as a discoloration and discontinuity which impairs the usefulness of the coating. Blush can be avoided if sufficient high-boiling solvent is present in the final stages of the drying process to redissolve the precipitated material. Blush-retardant thinners contain a high proportion of high-boiling active solvent which not only lessens the blushing tendency by reducing the drying rate and the resultant cooling of the applied film but also provides additional active solvent for redissolving any precipitated film material during the final stages of drying. Blush retarders must be used sparingly and with discretion because too much can upset the original solvent balance of the formulation and

create application difficulties (e.g., running, sagging, prolonged tackiness) while also affecting, sometimes adversely, the structure and properties of the film that is laid down.

Yet another reason for thinning an organic coating material is to replenish solvent lost through evaporation from the container while the material is in use or between usage. Normally, such adjustment is best made with a thinner the composition of which is essentially the same as that employed in the original solvent formulation. It should be recognized, however, that in the case of a composite thinner covering a range of boiling points, the bulk of the solvent loss will be in the lower-boiling constituents. Therefore, if the solvent loss has been excessive—as indicated by a pronounced increase in the viscosity of the paint in the absence of chemical reactivity—it is advisable that the restoring thinner be richer than normal in low boiling constituents. The problem of proper thinning is most difficult with critically balanced complex solvent formulations such as those used in lacquers and dopes; it is least critical with paints that utilize single solvents or simple blends of similar solvents, such as the turpentine and/or mineral spirits which constitute the volatile portion of oil-base or oleoresinous paints.

5.3.2.1. PRINCIPLES OF PROPER THINNING.—Whether the purpose of thinning be to reduce viscosity, retard blush, replenish lost solvent, or some other function, certain basic principles should be kept in mind to ensure satisfactory results. Every organic coating material is a specially formulated material designed for a particular type or area of service. The volatile portion of the vehicle has a major role in determining the solids content and application viscosity of the material, its drying rate, the structure and adhesion of the deposited film, and the resultant effects on appearance, mechanical properties, and durability. When the original material must be thinned, for whatever reason, the essential solvent balance must be maintained in order to obtain the desired film properties for which it was designed.

The principles and importance of proper solvent balance in determining the properties and performance of the coating may be seen from consideration of a typical lacquer formulation (the general characteristics of a lacquer are discussed in section 2.2.4). The nonvolatile portion of a lacquer typically may consist of the film-forming base, a modifying resin, a plasticizer, and possibly a stabilizer or other additive—plus suitable pigments where color or opacity are desired. The volatile vehicle is a mixture of active solvents (including latent solvents) and diluents, in a range of boiling points and associated evaporation rates. The active solvents are needed to dissolve the film-former and produce a solution of high solids content at the proper application viscosity. The diluents, although nonsolvents, are well-tolerated and serve to extend the solvents for economy while contributing to the adjustment of viscosity, drying rate, and gel properties. The amount of volatile liquid contained at the gel stage is an important factor in determining the structure of the film that is laid down as the residual liquid evaporates. In general, the low-boiling constituents of the volatile vehicle contribute solvent power and fast setting, the medium-boiling components control the drying rate to allow good leveling, the diluents (usually medium-boiling liquids) regulate the on-set of the gel stage, and the presence of some medium- to high-boiling active solvent imparts blush resistance and ensures solubility of the film-former in the final stages of the drying. To meet the concurrent and often conflicting requirements of (1) high solids content for good film build per coat at a workable viscosity, (2) good flow and leveling without runs or sags, and (3) fast drying without the development of film faults such as blush or cratering, it is essential to employ a suitably formulated mixture of active solvents and diluents carefully balanced for proper solvent power, evaporation rate, and gel stage composition.

To ensure that the performance characteristics so painstakingly built into the original formulation will not be nullified by improper thinning, the following principles and precautions should be observed:

(1) Use thinners only when specified or necessary, and in the minimum amount that will do the job. Even an ideal thinner may adversely affect the application properties, spreading rate, and ultimate durability of the coating if used where it is not needed.

(2) Whenever possible, use only that thinner or type of thinner which is specifically recommended by the manufacturer of the coating material.

(3) When the manufacturer's thinner, or a known substitute, is not available, make sure that the thinner to be used is completely compatible by adding it to a test quantity of the original coating material and noting if any flocculation, separation, or other abnormality occurs in the thinned paint and in a film prepared from it.

(4) In choosing or preparing one's own thinner, use a composition approximating that of the volatile vehicle of the original coating material. Compositional information, if not available from the label, may usually be obtained from the covering specification. Federal specification thinners for various types of coatings are listed in section 8.1.9.

(5) If the composition of the volatile vehicle is not known and its nature cannot be inferred from its odor, prepare a thinner on the basis

of known solvents and nonsolvents for the film-forming resin, keeping in mind the formulating principles previously discussed. (Information on the solubility of resins is available in chapter 3). If the identity of the resin base also is not known, then trial and error testing of small batches with various classes of solvents may reveal a compatible solvent for emergency use.

(6) Before thinning, thoroughly mix the original coating material to a uniform consistency as described earlier, add the necessary amount of thinner, and again stir to a uniform consistency.

(7) When using thinners, observe all due precautions against fire and toxicity hazards as described in section 5.2.

5.3.3. Activation of Two-Package Systems

Two-package coating systems are those in which the film-forming resin and the curing or hardening agent are furnished in separate containers for mixing just prior to use. Typical two-package systems include amine-cured epoxy resins, styrene-plus-peroxide-cured polyesters, amine- or polyol-cured polyurethanes, and metallic oxide-cured neoprenes and chlorosulfonated polyethylenes. Of these, the epoxies, polyesters, and polyurethanes cure at room temperature whereas the last two are usually heated after the catalyst or accelerator has been added.

Activation of two-package systems poses no special problems if the following precautions are taken:

(1) Many of the catalysts or curing agents employed are toxic prior to incorporation into the resin; in such cases, inhalation, skin contact, or ingestion should be avoided.

(2) It is important that the two components be uniformly mixed in the proportions recommended by the manufacturer to achieve optimum film properties.

(3) The activated mixture has a limited pot life—usually from one to eight hours, depending on the amount of catalyst used, the temperature, and the nature of the materials involved. Follow the manufacturer's instructions.

(4) The curing reaction frequently is exothermic; hence the coating may seem quite thin or be too thin for some applications shortly after being activated, because of the viscosity reduction resulting both from the addition of liquid reagent and from the temperature rise. In the case of epoxy resins, for example, an induction period of about 45 minutes after addition of the catalyst is recommended before using the coating material.

(5) In some instances, the thickness of the deposited film has a marked effect on the rate and extent of the cure achieved. Polyester coatings, for example, may not cure satisfactorily in thicknesses of less than six mils (0.006 inch) because of excessive loss of volatile catalyst, air inhibition, and reduced reaction temperature because of loss of the heat generated by the exothermic reaction.

(6) As a rule, follow the manufacturer's mixing and application instructions and take the recommended precautions.

5.4. Application Methods and Equipment

The choice of an appropriate application method from among the many available for applying organic coatings depends on a variety of factors, including the nature of the coating material, the type and texture of the surface on which it is to be applied, the shape and size of the object or area to be coated, environmental considerations, the available equipment and facilities, the skills available, fire and toxicity hazards, the time factor, and—last but not least—labor costs.

Obviously, the choice of method also depends upon an awareness of what methods are available and upon a knowledge of the technique involved and the advantages afforded by each. Detailed information about the commonly used methods of brushing, spraying, dipping, and spreading is readily available in many published books, manuals, pamphlets, and specifications [81, 96, 122, 154]. Similarly, detailed instructions for use of the newer or less well-known methods, such as airless spray and fluidized bed, are provided by the manufacturers or

suppliers of such equipment. Therefore, in the interests of adequate yet concise coverage, the objective in the sections which follow is to present the essential details of each method and to provide a sound basis for the *selection* of an appropriate application method. Toward this end, there is given for each method a description of the principle involved, the basic techniques and tools or equipment required, the main advantages afforded, and the chief limitations.

In general, application in the field is limited to brushing, rolling, and conventional cold or hot spraying methods, while factory coating operations are generally accomplished with more elaborate types of spraying (electrostatic, airless, etc.) or by special techniques such as fluidized bed.

5.4.1. Brush Application

Applying paint by brush is an ancient technique that still is used for a substantial portion

of the painting done in the field. While considerably slower than spraying, it gives excellent results when done with skill using the proper brush and technique. Brushing works the paint into pores and crevices in a way that spraying does not accomplish. At the same time, the brushing works surface dust and foreign matter into the paint, in effect cleaning away surface contaminants and thereby promoting good adhesion. For this reason, brushing is generally the preferred method of applying primers, especially on rough or imperfectly cleaned surfaces.

A high-quality brush of the proper size and shape is essential for good work. In the long run, the best brush—though initially expensive—is the most economical. The best brushes of today are made of specially selected Chinese hog bristles, sorted and bundled by skilled craftsmen to produce a quality tool. The bristles of such brushes have split or flag ends which are indispensable for holding an adequate quantity of paint and distributing it smoothly over the surface; the bristles continue to split as they wear down, thus maintaining their efficiency. Good nylon brushes with bristles having artificially flagged ends are also available; while they do not have the lasting paint-holding and brushing quality of the best bristle brushes, they will outwear bristle about four-to-one and are particularly useful for painting rough surfaces such as brick and cinder block. Nylon brushes are useful also with water-thinned paints because they are unaffected by water which tends to make bristle brushes soggy and less workable; however, they are not suitable for applying lacquers because the synthetic bristles may be attacked by the strong solvents used in these formulations.

A high-quality paint brush is an expensive tool that deserves proper care to maintain its usefulness. A new brush should be broken in before use by shaking and combing it free of loose hairs and dust, soaking it in linseed oil for a day or two, and finally rinsing it in paint thinner. The brush should be suspended so that the bristles do not rest on the bottom of the container during soaking. When painting, the brush should not be used sideways or forced into corners or tight places; such abuse will ruin its shape and destroy its efficiency. Brushes are available in a wide variety of sizes and shapes and textures for almost any paint job. After each use, brushes should be cleaned thoroughly with a suitable thinner and stored in a clean place; if stored in oil or thinner between usage, the brush should be suspended as mentioned above (also see section 5.1).

Brush application of paint is a skill that must be acquired by practice and experience; nevertheless, certain basic principles should be followed. The paint should be brushed on in one direction, then cross-brushed. Oil-base paints should be brushed out thoroughly. Quick-drying paints should be brushed only enough to spread them evenly. Very quick-setting coatings such as lacquers must be applied quickly in only two or three strokes to avoid disturbing the gelled film—for this reason, lacquers are usually applied by spraying or dipping rather than by brushing. Near the end of each stroke, the brush should be gradually lifted to prevent roughness and brush marks. The paint should be stirred frequently during use to avoid settling. Since brushing "works" the paint, it is essential—to avoid lifting—that an applied coat be thoroughly dry before brushing on another coat.

5.4.2. Roller Application

The roller applicator is a fast and convenient (and therefore economical) means for applying various types of pigmented coatings to large, flat surfaces that are reasonably free of interference from architectural protrusions and mounted fixtures. It gives excellent results on porous or textured surfaces such as brick, cinder block, and plaster. And it is one of the best methods available for painting wire fence and grillwork. While it does not lend itself to the fine workmanship that can be achieved with skilled brush application, the roller is an excellent and proven tool which is capable of good results in the hands of either the skilled painter or the do-it-yourself-er. The roller applicator may be used with oil paints, alkyd enamels, latex paints, and various other synthetic resin-base coatings that do not set up too quickly. Quick-setting materials such as lacquers cannot be applied by roller.

The usual roller consists of a metal cylinder or cylindical frame that rotates on an axle supported at the ends by a frame to which a handle of any convenient length is attached. The cylinder is covered with a replaceable "sweater" of a suitable napped material—usually wool, mohair, nylon, or acrylic fiber. Covers for virtually any type of job are available. For use with water-base paints, a type of roller cover is available in which the napped material is bonded to a stiff hollow core of a suitable plastic or a resin-impregnated cardboard which can be easily slipped on and off the roller frame. The length and texture of the nap or pile are of prime importance in determining the application properties of the tool. Rough surfaces require long-nap roller covers. The longer the nap, the more the amount of paint that can be held, and the greater the stippling or "orange peel" effect. Wool covers hold more paint than other kinds and produce an attractive stipple that makes them preferred for most interior painting of walls and ceilings with oil- or alkyd-base

paints. Lamb's wool covers with naps of various lengths are used for both smooth and rough surfaces—a ¾-inch nap gives good results on light stucco or rough plaster. Mohair covers are used where a particularly smooth finish is desired, as in the application of gloss or satin enamel. Covers of nylon and acrylic pile are useful with latex paints because they do not mat or wilt when water-soaked; they also wear well when used on rough-textured surfaces such as masonry. Care should be taken not to use synthetic resin covers in strong solvents that may attack them. Polyester resins can be efficiently applied with roller covers of wool frieze (having a shaggy pile).

Types of rollers are available which carry a supply of paint inside the cylinder, the paint feeding through the napped cover as it is used; however, it has been difficult to achieve a uniform flow of paint by this method, and it has not found wide favor. Pressure feed also has been used—with the paint fed from source to roller on a continuous basis through flexible hose; this method also has found only limited application, mainly for coating very large areas.

In the conventional or dipping method of roller application, the coating material is placed in a tray having a sloping bottom, and the roller is dipped into the tray and rolled back and forth until it is loaded with the paint. Excess paint is rolled out on the grid of the dip tray, and the paint is then applied to a strip of surface by rolling back and forth *slowly* until complete coverage is obtained. Rolling should not be continued too long, lest the paint set up and be ruined. During roller application, adjacent strips should be lapped as in other methods of painting. Since the roller will not fit into corners, the edges of walls and ceilings must be painted ("cut in") by brush before beginning the roller application. The roller should follow the brushing promptly to avoid lap marks.

To keep rollers and covers in good condition, it is essential that they be thoroughly cleaned after each use by squeezing out excess material and washing in a suitable solvent. Latex paints can be washed out with soap and water, with thorough rinsing. Roller covers should be dried on their rollers to avoid shrinkage. Wool covers may be combed while damp to minimize matting.

5.4.3. Spray Application

More paint is applied by spraying than by any other method because of its general applicability to most painting situations, and because of its speed and resultant savings in time and labor costs. Spraying is particularly convenient for overhead work, for large areas, and for reaching into areas inaccessible to brushing. When skillfully done, it produces a coating of uniform thickness and appearance unobtainable by brushing. Since the paint is merely laid on without being worked into the substrate, it is essential that the surface be clean to obtain good adhesion.

Successful spray painting is dependent on skill developed through knowledge and experience. Although a variety of different spray methods are available, all require clean paint, clean equipment, and a basically similar movement of the gun. The gun should be held perpendicular to the surface at all times, at a distance of six to ten inches, and should be moved in a straight line at uniform speed, with proper "triggering" at the beginning and end of each stroke. Proper triggering consists of starting the stroke before the trigger is pulled and releasing the trigger just before the end of the stroke to prevent the build-up of excessive amounts of paint at the beginning and end of each pass. Care should be exercised not to tilt the gun or move it through an arc; both these faults will result in a distorted spray pattern and a non-uniform coating. Arcing of the gun can be avoided by proper wrist action and body motion. Correct lapping is very important in achieving a uniform thickness and appearance. The lapping should be done in such manner that the center of the spray strikes the bottom of the previous pass. Corners should be sprayed by directing the gun toward the corner at a 45-degree angle to each side so that both sides of the corner are equally coated at the same time as the gun is moved along the corner (on vertical corners, the gun must be turned on its side—the idea is to utilize the long dimension of the elliptical spray pattern for accomplishing the double-edged coating operation).

The chief disadvantages of conventional spraying methods are those associated with the overspray caused by air and paint rebound from the surface being painted. The overspray wastes paint, necessitates the careful masking of adjacent areas, may contaminate surrounding objects (at a considerable distance when wind-borne), and may build up dangerous concentrations of toxic or flammable vapors and mists (see section 5.2 for Safety Precautions). To minimize these drawbacks, new methods such as electrostatic and airless spraying have been developed and are coming into widespread use, particularly for factory and industrial painting operations.

Both conventional and newer methods of spray application are described in the subsections which follow.

5.4.3.1. CONVENTIONAL COLD SPRAY is the application method most widely used in the field. While possessing the disadvantages

associated with overspray (see above), the method is fast and economical compared to brushing, especially on large jobs or rough surfaces. The equipment required is relatively simple and inexpensive compared to that of more elaborate methods. A typical system consists of an air compressor capable of providing up to about 90 lb/in^2 at the gun, an air transformer to regulate the pressure to the gun while filtering out dust and dirt and trapping out oil and water, flexible hosing to carry air and paint to the spray gun and its attached reservoir, and the spray gun itself. The latter is provided with an on-off trigger and with means for adjusting the flow of air and fluid to the spray head to obtain a desirable flow rate, proper atomization, and the desired spray pattern. The spray head is a removable assembly that includes a fluid-controlling needle, a hollow fluid tip, and an air cap. The fluid tip and air cap are chosen to suit the viscosity and solvent balance of the coating to be sprayed; it is essential always to use the type of fluid tip and air cap specifically recommended for the material to be sprayed.

Before spraying, the coating material should be thinned in accordance with the manufacturer's instructions, and the air and fluid pressures at the gun should be set and balanced to give an adequate flow of material with proper atomization and a normal spray pattern. If the ratio of air pressure to fluid pressure is too low, the spray pattern may be too heavy at the center or splotchy due to insufficient atomization. Too high an air-to-fluid pressure ratio results in over-atomization with the production of excessive fog and mist during the spraying operation. Misting can also be caused by holding the gun too far from the surface being sprayed, with the result that the paint particles become too dry enroute and are blown off the surface as a powder instead of adhering to it and coalescing. The thinner the liquid, the lower are the air and fluid pressures required for spraying; however, a material should never be thinned more than is recommended merely to make spraying easier—excessive thinning can produce its own quota of serious film faults, such as runs, pinholing, cratering, and blushing. Overspray can be reduced by using the lowest atomization pressure that will do the job satisfactorily. As a general guide, the common paints and enamels are usually sprayed satisfactorily at air pressures of 60 to 70 lbs/in^2 and fluid pressures of 15 to 20 lb/in^2, while lacquers and other low-solids liquids may be sprayed at air pressures of 40 to 50 lb/in^2 and fluid pressures of 10 to 15 lb/in^2.

The techniques to be used in spray application have been discussed in the introductory portion of section 5.4.3.

5.4.3.2. AIRLESS SPRAY is one of the recent developments in methods of spray application. Hydraulic pressure rather than air is used to accomplish the atomization of the coating material, in much the same way that a water spray is produced at the nozzle of a garden hose. High pressures—around 2500 lb/in^2—are required to force liquids of paint viscosity through the very small, precision orifice employed. Nozzles, valves, hoses, and other parts must be designed to withstand high pressure and erosion; hoses are usually lined with Teflon and wrapped with wire; nozzles are often made of tungsten carbide. A spray pattern similar to that obtained in air atomization is produced by a precisely milled slot on the face of the orifice. The high pressure required is usually generated by an air-powered fluid pump having a high fluid-to-air pressure ratio that permits hydraulic pressures of 2500 lb/in^2 to be obtained with only about 100 lb/in^2 of air pressure at the input. The compressed air serves only as a safe and convenient source of power for driving the fluid pump motor; air does not contact or become incorporated into the coating material.

The coating material is carried to the gun by a single hose; the flow is controlled by an ordinary high pressure valve. The gun itself does not have a trigger and has no means for varying the spray pattern; however, a variety of spray caps for use with materials of different viscosities are available. Once the air pressure to the fluid pump has been adjusted, the flow of coating material to the gun is controlled only by the valve, which must be turned on and off at the beginning and end of what is essentially a continuous spraying process. Although the problem of balancing air and fluid pressures is not present, the lack of fine control over the spraying process reportedly results in a rougher film than that obtainable by conventional spray. Airless spraying is therefore better suited for applications where protection rather than appearance is the paramount concern, and it is most feasible where relatively large surfaces and objects or a continuous production line is involved.

Both portable and fixed types of airless spray equipment are available. Also, airless spray may be combined with hot spray techniques (see section 5.4.3.3) to permit spraying at lower pressures through a triggered gun. With hot airless spray, the paint must either be recirculated between gun and reservoir or the feed hose must be hot-water jacketed all the way to the gun in order to maintain the required temperature and viscosity. (At least one manufacturer of hot airless spray equipment identifies his process by the term "airless spray" alone.)

The chief advantage of airless spray over

conventional spray lies in the great reduction in overspray achieved by elimination of the atomizing air. Since most of the sprayed paint stays on the surface to which it is directed, better coverage is obtained, paint waste is minimized, fog and mist are virtually eliminated, and the hazards of toxicity and fire are considerably reduced. With less solvent lost between the spray gun and the surface, the coating reaches the surface in a more fluid state, and most coating materials can be sprayed at package viscosity without the time and expense of thinning. Highly viscous materials may be difficult to atomize by airless spray. Also, coatings containing particles too large to pass through the orifice of the gun (e.g., fiber-containing paints and most multicolor lacquers) cannot be sprayed by the airless method. However, with most materials, a high rate of application and high film build per coat are possible with airless spray.

Because of the operational convenience, speed, and economy of airless spray, it is finding wide use in industrial finishing and maintenance painting.

5.4.3.3. HOT SPRAY, in which the coating material to be sprayed is first heated to a temperature in the vicinity of 150-175 °F, (66-79 °C), is applicable to both airless and conventional spraying techniques. The paint is safely and rapidly heated by passage through a hot water heat exchanger supplied from a directly heated boiler and is carried to the gun by a heated hose. Heating reduces the viscosity of the material, lessens the amount of thinner required, and permits spraying at a higher solids content. The result is heavier film build per coat, with attendant economy of time and labor. Hot spray is accomplished at lower pressures than conventional spray, with a considerable reduction in the amount of overspray and its accompanying evils. The higher spraying temperature and lesser amount of thinner to be evaporated virtually eliminate the tendency toward blushing, even under adverse humidity conditions, so that year-round spraying is possible.

Coatings for hot spray application must be specially formulated for proper solvent balance and viscosity; otherwise, the coating may suffer from poor coalescence, dusting, pinholing, and other defects. With proper formulation (e.g., elimination of fast-evaporating solvents), hot spray coatings are less prone than conventionally sprayed coatings to such defects as running, sagging, orange peel surface, etc.

5.4.3.4. FLAME SPRAYING is a technique that permits thermoplastic materials that are insoluble in organic solvents to be applied to metal and other surfaces. The coating material in the form of a powder is almost instantly liquefied as the resin particles, suspended and propelled by compressed air, emerge from the flame-ringed nozzle of a specially constructed gun. Upon striking the surface, the liquefied resin particles immediately "freeze" or congeal into a continuous coating.

Although the flame-spraying technique has been used chiefly for applying polyethylene coatings to metal surfaces, the technique is applicable to other thermoplastic resins (e.g., fluorocarbons and polysulfides) which are chemically stable at their melting point for the brief second during which the resin is in the liquid state. Metal surfaces permit the option of heating the surface also, when practicable, to achieve better coalescence and a smoother film. Coatings applied by flame-spraying to clean, properly prepared surfaces adhere quite well and provide a means for utilizing as coatings a number of highly chemical-resistant resins which cannot be conveniently applied by solution or dispersion techniques (the latter requires fusing, which may not be feasible in some applications).

5.4.3.5. ELECTROSTATIC SPRAY utilizes the attraction between electrically charged materials of opposite polarity as a basis for the rapid application of uniform coatings, even on complex shapes, with a minimum of overspray. The coating particles are charged to a high negative potential (up to 100,000 volts) as they contact or pass through a suitably shaped electrode. The object or surface to be coated is grounded, so that it is effectively at a high positive potential with respect to the negatively charged coating particles. The atomized particles are therefore drawn swiftly to the surface and captured, with very little overshoot even on objects with an open structure. The method requires that the coating material be essentially nonconductive so that its charge will not be dissipated by current flow between particles, and that the surface to be coated be electrically conductive enough to remain at ground potential so that its attraction for the negatively charged particles can be maintained.

Several different methods of electrostatic spraying are available. While all utilize the basic principle of electrostatic attraction by giving the coating particles a high negative charge while maintaining the surface at ground potential, they differ in the manner in which the coating material is atomized and directed. Also, the original use of electrostatic spray for applying liquid coating materials has recently been supplemented by an electrostatic method for applying dry powder coatings.

5.4.3.5.1. *Liquid electrostatic spray* may be of the air-atomized type or the airless type. A conventional spray gun is used in the air-

atomized type but is operated at the lowest pressure (about 12 lb/in²) that will atomize the paint and start it from the gun. The atomized coating material is sprayed into a negatively charged field where the particles too become negatively charged and are drawn to the grounded (effectively positive) object to be coated. The conventional spray gun permits triggered control of the spraying process.

5.4.3.5.2. *Airless electrostatic spray* uses either centrifugal methods or hydraulic pressure to atomize the coating material, and the material is applied in a continuous rather than a triggered operation. In a typical centrifugal method, the paint is pumped from a small hole in the center of a negatively charged spinning disc that imparts a similar charge to the paint. The paint becomes atomized as it is thrown from the edges of the fast spinning disc. The charged particles are then drawn to the grounded objects which are positioned in a circle around the spinning disc. The objects may be slowly rotated while the disc is moved up and down to provide complete coverage on all sides. In another centrifugal method, the paint is fed into a negatively charged spinning bell that gives the paint a negative charge and directs the atomized particles driven from its rim toward the grounded object to be coated. The centrifugal methods are useful chiefly for industrial finishing, where the necessary spray equipment and automatic positioning and conveyor facilities can be set up on a permanent basis.

The most widely applicable method of airless electrostatic spray combines the normal airless spray technique discussed in section 5.4.3.2 with the electrostatic principle described in this section. Here, the negatively charged coating material is atomized by hydraulic pressure as it leaves the orifice of the airless spray gun and the charged particles are drawn to the grounded (positive) surface to be coated by electrostatic attraction as before. This method is adaptable for field application as well as for industrial finishing.

All wet electrostatic spray methods afford similar advantages of minimum overspray with a great reduction in the hazards, waste, and inconvenience normally associated with overspray, together with substantial savings in time, material, and labor costs compared to conventional methods of application.

5.4.3.5.3. *Dry electrostatic spray* is a comparatively recent development [74] in which the coating material is sprayed in the form of a dry powder that goes on as a one-hundred-percent-solids coating. The powder is charged to a high negative potential (about 90,000 volts) and then fed at very low air pressure (about 1 lb/in²) through a spray nozzle. The charged particles leaving the nozzle are attracted to any electrically grounded object in their general path and will adhere to the surface long enough to permit a heat cure that fuses the particles into a continuous film. Uniform coatings up to 20-mils thick can be applied in a single pass of the spray gun, even on complex shapes. Objects with open structures, such as wire mesh and fan guards, can be coated on both sides at the same time by using an ungrounded surface on the far side as an electrostatic reflector to repel particles back to the object. An application rate equivalent to laying down a three-mil-thick coating at the rate of one square foot per second is possible.

Since the coating is all solids, the fire and toxicity hazards and the expense of volatile solvents are completely eliminated. Spray booths are not needed, and the method is well suited for either field or factory application. Despite the high voltage employed, the method is completely safe because of the very low current involved (only 0.2 milliampere). Any type of powder that is essentially nonconducting can be sprayed onto any surface that is at least mildly electrically conductive. Thermoplastic (heat-fusible) materials such as polyvinyl chloride, cellulose derivatives, fluorocarbons, polyethylene, and polypropylene are readily applied by this method; however, the method is applicable to thermosetting resins such as epoxies only if a curing agent inactive at room temperature but effective when heated can be incorporated into the material. Inorganic fusible powders such as talc, vitreous frit, and metallic oxides also can be applied by dry electrostatic spray. Surfaces that have been successfully coated include metals, glass, heated plastics and ceramics, and moist paper and cloth.

It may be noted that the dry electrostatic spray process is most useful with many of the same resins employed in the fluidized bed technique (see section 5.4.6). However, large objects (e.g., automobile bodies) are more easily coated by electrostatic spraying, and thin coatings can be applied with a greater degree of uniformity.

5.4.3.6. DUAL-GUN SPRAYING provides a practical means for spraying two-component coating systems that must be activated at the time of use and have only a limited pot life after activation. Epoxies, polyesters, and polyurethanes are typical of the coating materials that are being successfully applied by the dual-gun technique. Such materials cannot be applied by conventional spray gun because their continually changing viscosity makes them difficult to control, and the gun would be capable of only limited operation before it would have to be thoroughly cleaned to avoid permanent clogging with hardened resin. Specially designed

dual spray guns are now available [63] that are capable of continuously metering and mixing the two components (resin and catalyst) in the correct proportion at the instant of spraying. Resin and catalyst are fed to the spray gun through separate hoses, one or both of which may be heated if necessary to reduce the viscosity of the material. Built-in metering devices of almost any needed precision deliver the two materials to a chamber in the spray head, where they are intimately mixed in the exact proportions required for proper cure and then sprayed from the orifice under sufficient hydraulic pressure to produce atomization (cf., airless spray, section 5.4.3.2).

5.4.4. Dipping and Flow Coating

5.4.4.1. DIPPING is a fast and economical method of industrial finishing—one that lends itself to a continuous conveyorized operation from initial cleaning of the surface to final curing of the coating. Despite the seeming simplicity and ease of dip coating, it is actually a difficult process because of the many variables that must be closely controlled to obtain a satisfactory finish. Because of these difficulties, combined with the need for a relatively large volume of material in the dip tank, dipping is not usually a convenient or economical way of coating objects in the field, especially on an intermittent or sporadic basis.

Of basic importance in determining the thickness and uniformity of the coating are the composition and viscosity of the coating material, the rate of withdrawal of the object, and the effectiveness of the drainage in preventing drips and fat edges in visible areas. Control of viscosity requires control of both temperature and solvent evaporation in the dip tank. Loss of solvent does not merely raise the viscosity; through the differential evaporation of lower-boiling constituents, the solvent balance also is changed—and along with it the drying and drainage behavior of the coating. Adding more of the original thinner can restore the proper viscosity but does not restore the original solvent balance. In industrial finishing, a practical remedy for the evaporation problem is to maintain a nearly solvent-saturated atmosphere in the dipping room; however, this greatly increases the risk of fire and requires every possible precaution against sparks and flame. Water-thinned coatings are free from the problems of differential evaporation and fire hazard but may introduce coverage and drainage problems of their own.

The shape and surface texture (e.g., porosity) of the object and the rate of its withdrawal from the dip tank have a direct effect on drainage and on the thickness and uniformity of the coating. The faster the object is withdrawn, the greater is the thickness (up to a certain point), and the less uniform the coating tends to be. In general, best results are obtained by withdrawing the object at a slow, uniform speed that permits most of the drainage to take place as the withdrawal proceeds. However, when a second coat is to be applied on a material that is quickly attacked by the solvents in the formulation (as happens with many lacquers), it may be necessary to perform the dipping quickly to avoid redissolving some or all of the previous coat.

The dip tank should be no larger than is necessary to accommodate the object and should have a minimum cross-sectional area to minimize solvent evaporation and coating deterioration. An agitator should be provided for the continual stirring of pigmented materials. Clear coatings should be stirred occasionally and whenever the material in the tank is replenished. The tank should be kept covered when not in use to reduce the fire hazard.

5.4.4.2. FLOW COATING is a process in which the coating material is flowed onto the object from a hose, after which the excess material is allowed to drain off into a shallow tank or drip pan and recovered for reuse. Flow coating is very similar to dipping in its requirements for close control of the coating composition, viscosity, drying rate, and drainage characteristics—but it has the advantage of not requiring a large dip tank. The coating material is supplied from a central reservoir which can feed several hoses at a time if desired, while permitting convenient sampling and control of the coating composition at its source.

In both the dipping and the flow coating processes, the manner in which the object is hung (particularly if it is of complex shape) is of the utmost importance in achieving a uniform coating without unsightly drip beads or fat edges.

5.4.5. Knife and Roller Coating

Knife coating and roller coating are high-speed industrial coating methods for applying a wide variety of coating materials to flat surfaces on a continuous production line basis. Both are essentially spreading methods.

5.4.5.1. KNIFE COATING is similar in principle to the doctor-blade technique used in the laboratory for the application of uniform films. It can be used for coating rigid, flat sheet material or for materials that can be held flat on a rigid substrate while being coated. Only one side can be coated at a time. The coating material is flowed on and spread evenly over the surface as the latter is drawn beneath the knife or doctor-blade. The coating thickness

will vary with nonuniformity in the thickness of the sheet stock.

5.4.5.2. ROLLER COATING utilizes hard rubber or steel rolls to apply the coating to flexible, flat sheet stock of metal, cloth, paper, and thin composition board. The coating material is applied and spread evenly over the surface of the material by a roller rotating in a direction opposite to that of the strip of material being coated, while the strip is held against the coating roller by tension furnished by the driving rolls. The coating roller receives its paint from a feed roll that dips into a paint reservoir as it rotates and then offsets the paint onto the coating roller. Coating speeds of fifty feet per minute are readily achieved. If desired, both sides of the strip can be coated at the same time. The method is not applicable to thick stock that will not bend over the rolls.

5.4.6. Fluidized Bed Coating

Fluidized bed coating is one of the recent innovations in the coatings field. It is a rapid, convenient, and economical method for applying solventless (100 percent solids) coatings on objects of metal, glass, ceramic, plastics, and other materials capable of withstanding the heating and fluxing temperatures involved in the process. It also makes possible the utilization of insoluble resins that cannot be readily applied as a coating by ordinary methods. The technique is particularly suitable for coating small objects and for applying thick, uniform coatings even on complex or undercut shapes. The method is applicable to both clear and pigmented coatings.

In the fluidized bed process, the coating material in the form of a fine (50–150 mesh) dry powder is "fluidized" by suspending the coating particles in a controlled upward stream of gas (usually compressed air or nitrogen). This is accomplished in a vessel that is divided into an upper and lower chamber by a porous membrane that retains the powder while permitting passage of the gas. The coating particles must be spherical in shape to present a uniform surface resistance in the gas stream and to avoid the agglomeration that tends to occur with irregularly shaped particles. Both powder and gas must be clean and dry to ensure free mobility of the particles. Their mobility is enhanced by a small electrostatic charge which keeps the particles apart. The fluidized powder occupies three to four times the volume of the original powder. A properly fluidized bed looks and behaves like a liquid and offers negligible resistance to the movement of an object immersed in it.

The article to be coated is preheated to a temperature above the melting point of the resin and then dipped into the fluidized bed, where it acquires a uniform coating of the material as the particles melt onto it. (Irregularly shaped or undercut objects should be moved through the bed to obtain complete coverage.) Upon withdrawal, the coating congeals into a more or less continuous film which may be further annealed in an oven to ensure good leveling and a pinhole-free coating and to complete the curing of a thermosetting resin. The coating thickness obtained depends on the preheat temperature, the shape of the object, and the duration of the dip. Thin-walled sections may present some difficulties because of quick cooling while in transit from preheat to dip. Since the object must be suspended while being dipped into the fluidized bed, an uncoated area is left at the point of suspension which can be touched up by filling it with powder and then fusing it with a blast from a hot-air gun.

While the fluidized bed method is most widely applicable to thermoplastic resins which are readily fused into a continuous film, it can also be used with thermosetting resins that can be liquefied by heat prior to being finally cured by after-heating; epoxy resins are a notable example. Thermoplastic resins which have been successfully applied by the fluidized bed technique include virtually insoluble resins such as polyethylene, polypropylene, nylon, and the fluorocarbons, as well as soluble resins such as polystyrene, vinyls, acrylics, and cellulosics.

When using the fluidized bed method, it should be borne in mind that the powdered material presents health and safety hazards unless adequate facilities are available for hooding, exhaust, and dust collection.
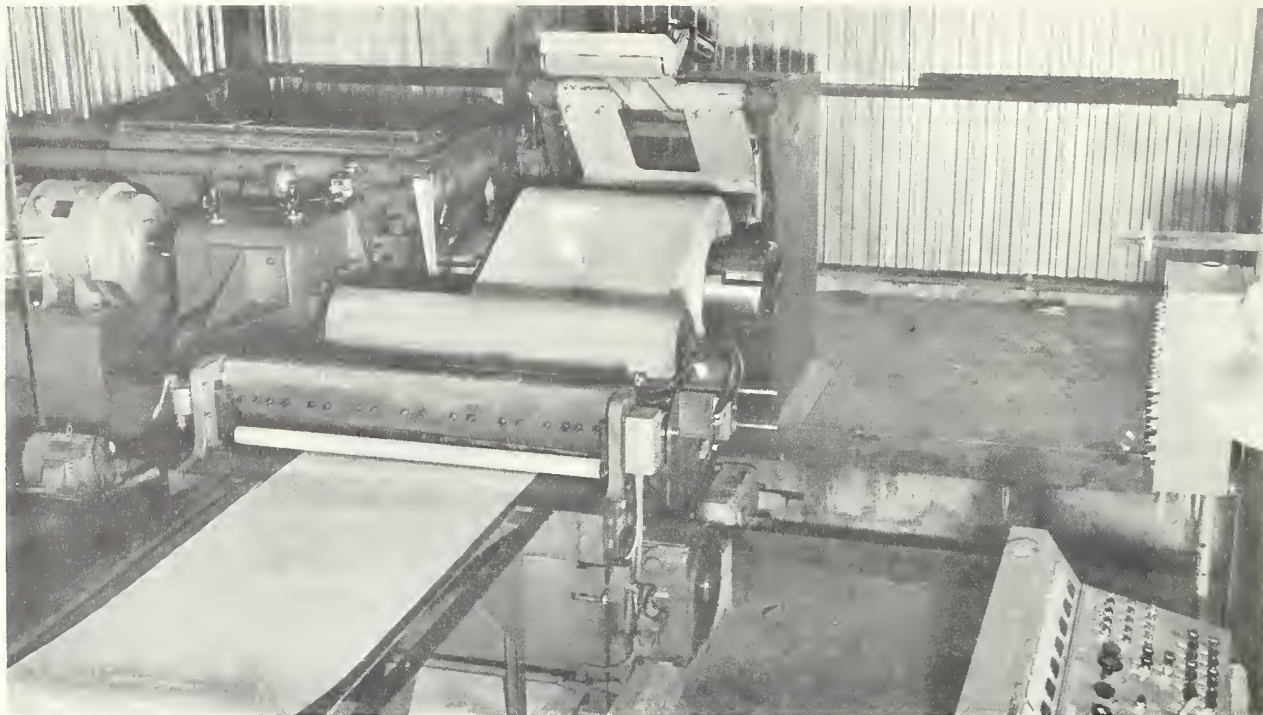
FIGURE 5.1. *Roller-coated sheet metal stock ("coil coating") passes through final inspection station to recoiling equipment.*
(Photo courtesy of Industrial Finishing.)

FIGURE 5.2. *Electrostatic spray gun paints chain link fence from one side with very little overspray.*
(Photo courtesy of Ransburg Electro-Coating Corporation.)

6. Surface Preparation and Pretreatment

The common denominator in all surface preparation is thorough cleaning of the surface. To the clean surface, pretreatments may be applied to enhance adhesion and (in the case of metals) to provide a barrier against the spread of corrosion. Whereas the purpose of the basic surface preparation is to achieve a physically clean surface, the pretreatment is a chemical process, the functions of which are: (1) to change the original surface to one that possesses a greater surface area and/or a greater specific affinity for the primer to be applied, and (2) in the case of metals, to passivate the surface and retard corrosion.

The choice of a practical method of surface preparation depends on the nature and condition of the surface, its size and shape, the equipment available, the type of coating to be applied, and the service environment. Methods range from light brushing or a simple solvent wash to heavy sandblasting. Dirty or corroded surfaces, coatings of limited wetting ability, and severe service environments require vigorous, thorough cleaning methods; for example, rusty steel that is to receive a phenolic coating system to withstand marine exposure must be thoroughly cleaned by sandblasting before the coating is applied if good service performance is to be achieved. On the other hand, a solvent wash may suffice for an aluminum surface that is to receive a wash primer pretreatment; and new wood siding that is to receive an oil paint may need no cleaning at all (although knot-sealing and puttying of nail-holes may be necessary). The important point is that whatever method of surface preparation is selected must be suited to the job and thoroughly performed; skimping in either the selection or the execution of a method of surface preparation is an invitation to trouble.

A variety of chemical pretreatments, many of them of a proprietary nature, are available for use on specified types of surfaces. Pretreatments for metal find the widest use; they are based on various chemical agents, including phosphating, chromating, and oxidizing agents, formulated for maximum effectiveness on the particular metal to be treated. Pretreatments—usually in the form of acidic agents or resinous surface conditioners—are also useful on concrete and masonry surfaces. Plastics, particularly those with low energy (non-adherent) surfaces such as polyethylene and the fluorocarbons, may be treated with strong acid, caustic, or oxidizing agents to etch the surface for better coating adhesion.

In the sections that follow, the basic importance of proper surface preparation is stressed, and specific information on the preparation and pretreatment of various kinds of surfaces is presented.

6.1. Importance of Surface Preparation and Pretreatment

The importance of proper surface preparation to the durability of any coating system cannot be overemphasized. Without proper surface preparation, the finest paint—applied with the greatest skill—will fall short of its maximum performance capabilities or may even fail miserably. Considering the proportionately high cost of the labor involved in applying protective coatings as compared to the cost of materials, it would appear to be axiomatic that only the most durable materials applied in a manner that achieves maximum service should ever be used. Yet there are some who, while recognizing the value of high-quality materials and workmanship, fail to grasp the fundamental importance of surface preparation as the foundation upon which all else depends. There seems to exist in some cases a subconscious willingness to take a chance when it comes to the hard work of surface preparation. But while an attitude of "the old surface isn't going to show, so why should I bother with it" may be understandable in the unversed do-it-yourselfer, such misconception has no place in the workmanship of the professional painter or responsible coatings official.

A coating can provide its function only so long as it remains intact and firmly bonded to the surface it is to protect or decorate. Good adhesion requires that the coating material be brought into intimate contact with the surface itself (or a firmly bonded chemical pretreatment layer), without intervening corrosion products or contaminants, to permit the interaction of molecular forces of attraction directly between the coating and the substrate material. Thus, a properly prepared surface is essentially a clean surface, but not necessarily the ultimate in cleanness. It is frequently impractical, for economic reasons or because of equipment limitations, to achieve a perfectly clean surface; nor is this usually necessary. However, *adequate* surface preparation can and must be achieved in all cases if the coating is to adhere firmly and durably. An adequately prepared surface not only provides a good anchor for the coating but also ensures a surface free of corrosion products or contaminants which

might shorten the life of the film by spreading along the coating-substrate interface and destroying adhesion, or by actually breaking through the coating.

The value of chemical pretreatment, particularly for metals, lies in the thin, tightly adherent, ideally roughened, paint-receptive film that is formed on the metal surface. Not only does such a film provide an excellent base for coatings adhesion, but it also resists the spread of corrosion beneath it, so that damage to the substrate from a break in the film is not as likely to progress beyond the area of immediate damage.

6.2. Preparation of Wood Surfaces

6.2.1. Bare Wood

6.2.1.1. GENERAL. — Wood surfaces to be painted should be clean, free of cracks and splinters, and properly seasoned (moisture content below 15 percent for exterior wood, and less than 10 percent for interior wood). Excessive moisture in the wood is accompanied by large dimensional changes as it dries, which may cause cracking of the paint film; also, the entrapped moisture may cause blistering of the film, with early flaking or peeling. Green wood should be allowed to cure for at least a week in clear, warm weather before painting is attempted. Seasoned wood that has become wet should be allowed to dry until it is dry to the touch before painting.

Cracks and nailholes should be filled with putty or plastic wood. Puttying must be preceded by application of a primer to prevent loss of oil from the putty by absorption into the wood. The putty should be allowed to dry for at least 48 hours in the case of shallow holes or cracks, and for a period of from one to three weeks for deep fillings. Plastic wood— although more expensive and more difficult to handle than putty—may be used directly on the bare wood and hardens in a few hours. When dry, the filled areas should be lightly sanded before painting.

Loose dust, dirt, and sandings should be brushed away. Scraping or wire brushing may be used to dislodge mortar scale, pitch streaks, and other tightly adherent foreign substances. Grease and oil can be removed by washing with mineral spirits or white gasoline (caution). Shop markings may be removed by sanding or a solvent wash. Smoothing may be done with sandpaper, steel wool, or power sanding machines.

6.2.1.2. EXTERIOR WOOD should be properly seasoned, clean, and dry before painting. Although a smooth surface is not necessary, the wood should be brushed, scraped, washed, or sanded as may be required to produce a surface free of dust, dirt, oil, grime, sap streaks, splinters, projections, and very rough areas.

Knots require special treatment to minimize the possibility of discoloration, cracking, and premature failure of the paint applied over them. As much sap as possible should be removed from the knot by scraping and by washing with turpentine. When the area is dry a good knot sealer should be brushed on, such as the WP–578 knot sealer developed by the Western Pine Association and covered by Military Specification MIL–S–12935 [149]. This knot sealer consists of a ten-to-one blend of a phenolic resin and polyvinyl butyral in denatured alcohol solution. It has proven more effective than shellac or aluminum paint for this purpose.

The puttying of nailholes and cracks is an important part of the preparation of exterior wood surfaces for painting; however, it should be done after the priming coat has been applied and dried, as indicated in section 6.2.1.1. The putty should be allowed to dry thoroughly before the finish coats are applied.

6.2.1.3. INTERIOR WOOD should be well seasoned, clean, and dry when painted. It is essential that the surface be sanded to a smooth texture before painting to obtain a good finished appearance. The type and amount of sanding required depends on the initial roughness of the surface. To avoid unnecessary scratching or gouging of the wood with a resultant increase in the amount of labor ultimately required to achieve a smooth surface, sandpaper of the minimum coarseness that will do the job should be used. Where an initially rough surface is involved, sanding should start with a more or less coarse grade of sandpaper and proceed through intermediate grades to a fine grade for finishing. The sanding should be done in the direction of the wood grain.

Sanding of woodwork and cabinet work may be accomplished by starting with a medium grade sandpaper (No. 1) and finishing with fine sandpaper (No. 0 or finer). On furniture, or where the finest finish is desired, the final sanding should be done with a very fine grade of sandpaper (No. 4/0).

Fine steel wool may be used instead of sandpaper and is particularly useful on rounded or irregularly shaped surfaces.

Floors are best sanded by machine, working in the direction of the wood grain. For the first rough sanding, coarse sandpaper is used (No. 2½ for hardwood and No. 3 for softwood floors), followed by No. 1½ sandpaper, and finishing with a fine grade (No. 0) for hardwood and a medium grade (No. 1) for softwood (fine sandpaper becomes gummed by soft woods under power sanding conditions).

Wherever nails are used, they should be

countersunk and the nailholes filled with plastic wood or putty (the surface must be primed or sealed before puttying, as indicated in sec. 6.2.1.1). Plastic wood—although more difficult to handle than putty—is often preferred for its more natural appearance and quick-drying properties. As previously noted, putty may require days or weeks of drying before it can be painted satisfactorily. When thoroughly dry, the fillings should be sanded smooth before painting.

Where stain is to be used, the stain is applied directly to the bare wood surface. The stain, when dry, is followed by a wash coat (frequently one pint of shellac varnish thinned with four to seven parts of denatured alcohol) and given a further fine sanding. At this point, open-grain woods, such as oak and walnut, are given a coat of paste wood filler thinned to brushing consistency. The filler is allowed to set for about twenty minutes, and the excess is then removed by wiping *across the grain*. After the wood filler has dried, any remaining excess is sanded away, leaving the stained, filled wood surface ready for the clear finish coats.

6.2.2. Previously Painted Wood

The repainting of wood surfaces is most easily accomplished when it is done at the proper stage in the life of the coating—that is, when the coating is well-worn but still basically sound. At this stage, little if any surface preparation is required other than the brushing or washing away of loose chalk, dust, dirt, or grime. On the other hand, if the old paint is allowed to deteriorate to the point where large areas of the paint are flaking and peeling, or the paint is cracked and the edges curled, then it will have to be removed completely to prepare the surface properly for repainting. Complete removal of the old paint is a laborious, expensive task that must be accomplished with torches or paint removers, accompanied and followed by thorough scraping and sanding of the surface. Obviously, it pays to repaint at the proper time. This is best determined through periodic close inspection of the surface.

The preceding remarks are particularly applicable to exterior painted surfaces. Most white outside paints, and tinted paints to a lesser extent, are formulated to give controlled chalking of the coating which assists in keeping it clean. The ideal time to repaint such surfaces is when the paint is worn thin to the point where bare wood begins to show, or when minute checking and crumbling begin. Such surfaces take paint well and need little surface preparation. If chalking has kept the paint clean, brushing with a painter's duster may be all the preparation required. If chalking is excessive or if the old paint is soiled, washing with detergent followed by a thorough hosing down with water may suffice. In some instances, a final light sanding of the old paint may be desirable. Small deteriorated areas may be scraped, wire-brushed or sanded down to bare wood and spot-primed before over-all repainting. In such cases, the boundary of intact paint should be sanded to a feather edge.

If deterioration of the paint has progressed to the point where flaking and peeling, or widespread cracking and edge curling, have taken place, then the old paint will have to be entirely removed. On exterior surfaces, this is probably best accomplished by burning off the paint, with due precautions against the hazards of fire and toxic fumes (see sec. 5.2). The burning off should be done by an experienced worker. The paint is heated sufficiently to soften it and cause it to blister so that it can be removed with a scraper. Care must be taken not to char the wood surface. Finally, the wood will require sanding to complete its preparation for painting.

Where burning off is not practicable, scraping and wire brushing may be used to remove the old paint, although the process may be long and tedious. Liquid paint removers (such as those covered by Federal Specification TT–R–251 or Military Specification MIL–R–46073) may be used effectively; however, they are relatively expensive and difficult to handle, and repeated applications and scraping may be required. Liquid paint removers are more effectively utilized indoors, where burning off is not feasible, and where a smooth final surface is desired. They give best results when applied on horizontal surfaces; vertical surfaces require a viscous remover of the semi-paste type. The wax film that forms on the surface of the paint remover should not be disturbed, since its function is to seal in the volatile active solvents until they have done their job of softening the paint. The directions of the manufacturer should be carefully followed when using liquid paint removers. Since they nearly always contain toxic volatile solvents, adequate ventilation should always be provided during their use. When removal of the paint has been effected, the residual wax must be removed from the surface by washing with mineral spirits, followed by a detergent wash and thorough rinsing with water. (Wax-free solvent-type paint removers are available but are generally not as effective as the wax-containing types.)

After the basic surface preparation has been accomplished, nailholes, cracks, and other defects should be puttied (after priming) as in the case of initially bare surfaces.

Interior paint coatings, unless worn thin by abrasion or repeated washing, are usually repainted because they have become dull, dis-

colored, or dirty—or because a change of color is desired for decorative rather than functional reasons. Such surfaces are relatively easy to prepare for repainting. The most important requirement is that the surface be free of loose dirt and grease. Indoor surfaces often become coated with a film of grease or oil from cooking vapors and from contact with people or objects. The new paint will not adhere long to a greasy surface. All such contaminants should be removed by thorough washing, first with mineral spirits, then with a detergent, followed by thor-ough rinsing with water. If the old paint is glossy, it should be lightly roughened with sandpaper or steel wool to improve paint adhesion.

In all repainting, care should be taken not to build up too great a thickness by applying too many coats or by repainting too frequently. A thick paint coat is prone to cracking and chipping off because it becomes too rigid to follow the normal dimensional changes in the wood.

6.3. Preparation and Pretreatment of Metal Surfaces

The basic requirement in the preparation of metal surfaces for painting, as with other surfaces, is cleanness. However, the degree of cleanness which is practicable or necessary—particularly in the case of steel surfaces—depends on the condition of the surface, the type of coating system that is to be applied, the nature of the service environment, and the cost factor in relation to the improved durability to be expected from more thorough surface preparation. The choice of a suitable method of surface preparation also depends on the location, size, and shape of the surface to be painted, and on the cleaning equipment and facilities that are available. Structural steel often must be painted in the field, under conditions involving certain limitations of surface preparation and coating application. Industrial steel products coated at the factory can be prepared for painting by thorough cleaning and pretreatment processes that yield optimum results.

Before considering the detailed information given in the following sections on the preparation of specific types of surfaces, the reader should consult the general information in the introductory sections of this chapter on the basic importance and purpose of adequate surface preparation and pretreatment.

Because of the enormous tonnage of steel used in structural applications and manufactured articles, and because of the continual need for protecting this strong but corrosion-susceptible metal from damage under a wide variety of environmental conditions, the methods of surface preparation employed for steel encompass virtually the entire spectrum of available methods. We shall therefore describe the various basic methods of surface preparation in the discussion of steel surfaces which follows, and shall merely make reference to these methods as needed in subsequent sections dealing with other metals.

6.3.1. Cleaning of Steel (and Iron) Surfaces

Although sandblasting to "white" metal (often followed by chemical pretreatment) provides the optimum surface for painting structural steel, the labor and high cost of this type of cleaning is ordinarily justified only when maximum performance under severe service conditions is required. Maximum performance in difficult environments usually involves synthetic resin-base coatings of high durability but limited wetting power; such coatings require thoroughly clean (and often pretreated) surfaces to develop adequate and lasting adhesion. Examples of such coatings are the phenolic and vinyl paints recommended in section 4.3.1 for severe marine service and immersion conditions. Oil paints, on the other hand, although suitable only for mild exposure in ordinary atmospheric environments, possess inherently good wetting properties that permit their use even on incompletely cleaned steel from which it has not been practical to remove all surface rust and corrosion products.

While the wetting ability of the primer to be used is the immediate factor determining the degree of surface preparation required, the choice of primer in turn depends to a large extent on the requirements for compatibility and good adhesion of the topcoat. Therefore, the surface preparation actually depends on consideration of the coating system as a whole. As part of the information presented in chapter 4 on Selection of Coating Systems, the general type of surface preparation required or considered adequate for particular types of coating systems and service environments was indicated. In the present section, the details about the various methods of surface preparation and pretreatment are given.

6.3.1.1. SOLVENT CLEANING with organic solvents is a very effective method for removing oils, greases, waxes, shop markings, drawing and cutting compounds, and other solvent-soluble foreign matter from the surface to be painted. The removal of such contaminants is usually prerequisite to the effective use of mechanical methods for removing rust, mill scale, and heavy dirt encrustations that cannot be removed by solvent cleaning. Mechanical cleaning methods, short of sandblasting to

"white" metal, do not completely remove such oily contaminants and may spread them over the surface in a film that can seriously impair the adhesion and durability of the applied coating.

6.3.1.1.1. *Wiping, dipping, or spraying.*— Since organic solvents remove oils, greases, and waxes by dissolving them, the cleaning liquid soon becomes contaminated with the removed products and must be purified or renewed to avoid redepositing an oily residue on the work when the solvent evaporates. This is particularly true when wiping, dipping, or spraying methods are employed; in these cases, it is essential that the final rinsing be done with clean solvent. The rather high cost of organic solvents, the large quantities required for solvent cleaning, the expense of solvent purification, and the need for precautions against fire and toxicity hazards combine to make organic solvent cleaning a relatively expensive though effective method of removing oily and waxy contaminants.

6.3.1.1.2. *Vapor degreasing* is the most effective and economical type of solvent cleaning; it is also the least hazardous. In the vapor degreasing process, the article to be cleaned is suspended in the solvent vapor above a boiling cleaning liquid (usually stabilized trichloroethylene or perchloroethylene, because of their virtual nonflammability and their relatively low toxicity as compared to other chlorinated hydrocarbons). The hot, distilled solvent vapors condense upon the relatively cool object, dissolving oils and greases and carrying them away as the condensed droplets fall back into the parent liquid. Cold water pipes or coils are often placed in the upper part of the degreasing tank or chamber to effect further condensation of vapor and to provide a vapor ceiling (above which vapors will not rise). The unique advantage of vapor degreasing over other organic solvent cleaning methods is that the article being cleaned is continuously washed with clean, distilled solvent, while the contaminants accumulate in the liquid below. Eventually, of course, the parent solvent must be purified by distillation, preferably in an auxiliary still, after first removing any undissolved water by a separatory process. To maintain an efficient degreasing operation, purification of the solvent should take place before the concentration of contaminants reaches about 25 percent. An incidental but important benefit of vapor degreasing is that the degreased work emerges warm and dry— and ready for any additional cleaning, pretreating, or finishing operations that are to follow.

Organic solvents do not remove corrosive salts, soaps, and other harmful water-soluble contaminants from the surface. These may be washed away with water, steam, detergents, emulsions, or alkaline cleaners.

6.3.1.2. STEAM CLEANING in combination with detergents, while comparable in cost to solvent cleaning, is an effective means for removing heavy soil as well as greases and oils from metal surfaces; it does not remove rust and mill scale. If a strongly alkaline cleaner is used, the action of the caustic together with the high temperature and high velocity of the steam will remove old paint as well as surface soil and grime. Steam and/or hot water at a temperature of about 300 °F (149 °C) and a pressure in the vicinity of 200 lb/in^2, and containing the desired detergent, is directed against the work from a distance of about six inches, with the nozzle tilted slightly in the direction of travel. Speed of travel, number of passes, and time between initial wetting and subsequent cleaning should be adjusted to the amount and nature of the soil to be removed. The time between initial passes and later return allows the detergent to act upon and loosen foreign matter to permit its complete removal during the final passes. Any alkaline residue remaining on the surface after the cleaning operation must be removed by thorough rinsing with fresh water. Steam cleaning is particularly well-suited for cleaning in the field, where the location, size, and shape of objects and structures frequently do not lend themselves to efficient cleaning by other methods. Workers engaged in steam cleaning operations should be protected against burns and chemical injury to the eyes and skin.

6.3.1.3. EMULSION CLEANING with emulsifiable solvents combines some of the cleaning action of both water and solvents. The emulsifiable solvents used are composed essentially of an organic grease solvent, an emulsifying agent, blending agents, and a petroleum thinner such as kerosene or mineral spirits. The work is immersed in the emulsifiable solvent (or the solvent may be brushed or sprayed onto the work) and allowed to remain for several minutes to dissolve oil and grease and to loosen dirt. The dissolved and loosened oil and soil are then emulsified and flushed away by a pressurized hot-water rinse. A small residue of emulsion usually remains on the surface and will leave a thin film of oil if not removed. Removal of this residue is readily accomplished by washing with steam, hot water detergents, or solvents. Cleaning with emulsifiable solvents permits removal of heavy oil and grease contamination at lower cost than with organic solvents alone; also, corrosive salts and other water-soluble contaminants are washed away during the pressurized rinse. Since most of the surface soil is emulsified and washed away

during the rinsing process, the emulsifiable solvent itself becomes contaminated only slowly and requires only occasional renewal. It should be kept in mind that the hydrocarbon solvents contained in these cleaners present the usual fire hazard associated with the use of organic solvents.

6.3.1.4. ALKALI CLEANING provides an economical and effective means for removing oil, grease, wax, corrosive salts, and other soil (except rust and mill scale) from metal surfaces. The strength of the cleaner can be varied from mild to caustic by varying the type and concentration of alkali employed. Among commonly used alkaline cleaners are trisodium phosphate, sodium tetraborate (borax), sodium meta- and ortho-silicate, sodium carbonate (soda ash), and—where maximum saponifying strength is needed—sodium hydroxide (caustic soda). Most proprietary alkaline cleaners employ blends of these materials to obtain a more versatile and more effective cleaning action; surface active (wetting) agents and emulsified hydrocarbon solvents are sometimes added to increase the grease-removing action of the cleaner.

Alkaline cleaners must be used hot (about 175 °F [79 °C]) for maximum effectiveness. They accomplish their cleaning action by saponifying oils and greases to form soluble soaps, and by loosening other types of soil by a detergent action that displaces the soil from the surface. The saponified oils and the loosened and suspended soil are readily flushed away by thorough rinsing with hot water. Strong alkaline cleaners based largely on sodium hydroxide are effective paint strippers for removing old paint from steel surfaces.

Alkaline cleaners may be utilized by immersing the article to be cleaned in a soak tank of hot cleaner, by pressure-spraying the cleaner over the object, or by an electrolytic process which generates gas bubbles that aid greatly in dislodging soil. Following the use of alkaline cleaners, care must be taken to rinse all alkaline material from the surface; even small traces of alkali, soap, or detergent left on the surface are detrimental to coating adhesion and durability. To ensure neutralization of any alkaline residue, a passivating dichromate or dilute chromic acid final rinse may be used, unless a phosphating or other suitable pretreatment is to follow.

While alkali cleaning is free from the fire and toxicity hazards of organic solvent cleaning (unless emulsified solvents have been incorporated), the corrosive effects of alkaline materials on the skin and on ordinary clothing must be guarded against. Caustic soda, in particular, can cause serious burns to the skin and eyes and is extremely irritating to the nasal and bronchial membranes if inhaled.

Workers should wear splash goggles, protective rubber gloves and garments, and respirators when preparing or using caustic solutions. In case of accidental contact of caustic soda solution with the eyes or skin, the affected parts should be flushed immediately with large amounts of water, and a physician should be consulted promptly.

6.3.1.5. ACID CLEANING or PICKLING is a very effective method for completely removing all rust and mill scale from steel surfaces by chemical and/or electrolytic action. The acids commonly employed are phosphoric, sulfuric, and hydrochloric—either singly or in combination. Occasionally, in special cases involving stainless or other alloy steels, hydrofluoric or nitric acid also may be used for brightening the surface or for scale removal.

6.3.1.5.1. *Phosphoric acid cleaning* is an excellent time-tested method for removing oil, grease, soil, corrosive salts, and light rust from metal surfaces. The phosphoric acid solution is combined with detergents and wetting agents to assist in soil removal and contains organic solvents such as alcohols and ketones to aid in the removal of oils and greases. Where heavy grease or oil contamination is present, it is desirable first to remove most of this by cleaning with organic solvents in order to avoid rapid fouling of the phosphoric acid cleaner. Although it is possible to remove even heavy rust and mill scale from steel surfaces by using hot, strong phosphoric acid pickling solutions (15–50% phosphoric acid) for a long period of time, it is preferable to employ a sulfuric acid pickling method (as described in the following section) for the efficient chemical removal of heavy corrosion products.

Cleaning with phosphoric acid solutions can be accomplished by dipping the work into a tank of the hot or cold cleaner, or by flowing or brushing the cleaner onto the work. After removal of soil and rust, the surface should be washed off with clean water (or wiped off with clean, damp rags if rinsing is not practical because of the size or location of the structure. Military Specification MIL–M–10578 describes two types of phosphoric acid metal cleaner, both of which must be diluted with three times their volume of water before use [78]. The type I cleaner, before dilution, contains about 47 percent by volume of phosphoric acid (85%), and is used where the surface can be washed off with water after the cleaning process. The type II cleaner, before dilution with water, contains about 14 percent by volume of phosphoric acid (85%), and may be used where washing with water is not practicable and the surface is merely to be wiped off with rags.

Unlike alkali cleaning or strong acid pickling,

phosphoric acid cleaning does not leave a harmful residue on the washed or wiped surface. Instead, the phosphoric acid gently etches the surface and reacts chemically with it to produce a minute layer of iron phosphate which provides both a mechanically and chemically receptive surface for subsequent coating. (The thin phosphate layer formed on the surface during phosphoric acid cleaning or pickling is not a substitute for—and should not be confused with—the heavy phosphating pretreatments which are described in sec. 6.3.2.)

6.3.1.5.2. *Pickling* with strong acids—usually sulfuric, but sometimes hydrochloric (muriatic) or other acids as already noted—is accomplished in dilute solution (usually at a concentration of 5 to 10 percent by weight) and at a temperature of 140 °F (60 °C) or above. Rust is readily dissolved by this treatment, forming ferrous salts which remain in solution. Mill scale is attacked more slowly; removal of mill scale is dependent largely on penetration of cracks and crevices by the acid which thus works its way beneath the scale where hydrogen is evolved and "blasts" the scale from the metal. The rate of rust and scale removal increases with increasing temperature, and with increasing acid concentration up to a certain point (about 50 percent by weight for sulfuric acid, and about 30 percent for hydrochloric acid). Adequate agitation must be provided to maintain a normal pickling rate. Inhibitors must be present in the acid bath to prevent excessive attack upon the metal itself in cleaned areas while rust and scale removal is still taking place in other areas; inhibitors also minimize surface bubbling and "hydrogen embrittlement" of the steel by controlling the amount of hydrogen evolved. The buildup of ferrous salts in the pickling solution slows down the rate of rust and scale removal; when this can no longer be compensated by increasing the temperature and acid concentration, the pickling solution must be discarded and a fresh bath prepared.

Before pickling is begun, oily contaminants (grease, wax, etc.) should be removed from the surface by solvent cleaning, alkaline cleaning, or other suitable degreasing method (see preceding subsections). After the pickling is completed, the work should be promptly and thoroughly rinsed with clean cold water; any acid residue will cause rapid rusting of the steel surface. The cold water rinse should be followed by a dilute dichromate, chromic acid, or phosphoric acid rinse to passivate the surface (chromium compounds should not be used if phosphate pretreatments are to follow; however, prompt treatment with dilute phosphoric acid is highly desirable in any event).

While pickling is an effective method for removing all rust and mill scale from steel, it is limited to objects that will fit into the available pickling baths. It is therefore largely a factory technique that finds its widest use on structural steel leaving the mill. Workers engaged in pickling activities must be carefully protected against acid splash or inhalation by wearing goggles, respirators, and suitable rubber clothing—including boots, gloves, and aprons.

Electrolytic pickling is more rapid than ordinary chemical pickling for removing mill scale because of the greater evolution of hydrogen and the resultant greater agitation and "blasting" action. There is little difference in acid consumption between the electrolytic and chemical processes, provided the latter is properly inhibited to avoid unnecessary solution of clean metal.

6.3.1.6. HAND CLEANING methods are suitable for removing loose rust, loose mill scale, dirt incrustations, and loose paint from metal surfaces that are to receive paints of good wetting ability (e.g., oil paints) that are destined for mild, noncorrosive atmospheric exposure. Hand cleaning usually suffices also for interior surfaces and for the spot cleaning and priming involved in most maintenance painting where the surface has not been allowed to deteriorate badly. Hand cleaning methods do not remove heavy or tightly bound rust and mill scale and therefore are not satisfactory where coatings of limited wetting ability (e.g., phenolic varnish paints) are to be used or where severe atmospheric exposure or water immersion conditions are encountered. Oil and grease, if present, must be removed by solvent cleaning (sec. 6.3.1.1) before commencing hand cleaning operations, since the latter may further spread oily contaminants over the surface.

Hand cleaning is accomplished with a variety of hand tools, including wire and stiff bristle brushes, scrapers (often with special shapes for reaching into difficult areas), impact and chipping tools such as hammer and chisel, and abrasive materials (emery cloth, sandpaper, and steel wool). Normally, chipping and scraping precede wire brushing. Finally, all loosened matter should be brushed or swept off and the surface blown clean with compressed air (vacuum cleaning also is suitable). Workers should be protected with goggles and dust respirators. If cleaning must be done in areas where flammable vapors may be present, nonsparking tools must be used to avoid the danger of explosion.

Since hand cleaning is slow and laborious (hence expensive) and of only limited efficacy, it is used primarily for small or noncritical jobs, for jobs that are inaccessible to power tools, where power tools are uneconomic or unavailable, where the surface is not very dirty or corroded (as in maintenance painting done

at the right time), and where the coating system to be applied can tolerate or overcome the residues remaining after hand cleaning.

6.3.1.7. POWER TOOL CLEANING removes little more dirt, rust, and mill scale than hand tool cleaning; however, it is less laborious and much more rapid. Like hand cleaning, it removes only *loose* mill scale and rust. (Blast cleaning—as described in the following subsection—is required to remove heavy rust and tight mill scale.) Since not all corrosion products are removed from the surface by power cleaning, the method is limited to coating systems that have good wetting ability for incompletely cleaned surfaces, or to coating systems that will not be subjected to severe environments or immersion conditions. Power cleaning is adequate also in most maintenance painting situations where the surface is in reasonably good condition and only spot cleaning to the bare substrate is necessary.

The tools required may be electric or pneumatic powered. They include large rotary power wire brushes, power grinding wheels and sanding machines, and power-driven rotary or piston type hammers and scalers for chipping and descaling. Of these, power wire brushes in a variety of sizes, textures, and shapes are the most widely used; cup shapes, radial types and disc shapes are available.

Oil and grease should be removed from the surface by solvent cleaning (sec. 6.3.1.1) before beginning power tool cleaning, to avoid spreading such contaminants over the surface. Chipping and scaling operations, if needed, should precede wire brushing. Great care is required, when using power impact tools, to avoid gouging sound metal. Excessive wire brushing of unremovable mill scale will burnish the surface and greatly reduce the adhesion of the applied coating. Areas not accessible to power tools should be cleaned by hand methods. After completion of the mechanical cleaning, all lossened material should be swept from the surface, and the surface should be blown clean with compressed air or cleaned by vacuum. Goggles and dust respirators should be worn for protection. If power cleaning must be done in areas where flammable vapors may be present, nonsparking motors and tools should be used to avoid the danger of explosion.

6.3.1.8. SANDBLASTING is a form of blast cleaning in which sand is employed as the abrasive which is propelled by compressed air through a nozzle directed against the surface to be cleaned. Other forms of blast cleaning utilize crushed iron grit (grit blasting) or iron shot (shot blasting) as the abrasive; these may use either compressed air or centrifugal wheels to propel the abrasive. Grit

blasting and shot blasting are very costly methods, the use of which is largely restricted to shop work or vacuum blasting where the expensive abrasive materials can be recovered for reuse; moreover, these methods usually yield a greater surface roughness (higher anchor pattern) than is desirable for most coating applications. The present section will be limited to a discussion of sandblasting as a most effective method of preparing steel and other surfaces for painting.

The height of the anchor pattern, or the maximum height of profile of a blasted surface, is the distance from the bottoms of the lowest pits to the tops of the highest peaks. The larger the size of the abrasive employed, the higher is the anchor pattern or the greater is the surface roughness produced. For good durability, the overall thickness of the dry coating must be great enough to cover even the peaks with an adequately thick protective film. Thus, surfaces that are to receive a thin coating require a shallower anchor pattern and hence must be cleaned with a finer abrasive than surfaces that are to receive a thick coating. Thicker coatings will not only tolerate a deeper anchor pattern but may benefit in adhesion and durability from the greater surface contact and better "tooth" provided by the rougher surface. There is, of course, a practical limit to the surface roughness that can be tolerated by films of practical thickness; peaks that are too thinly coated become focal points for wear and corrosion and premature coating failure. The effectiveness of sandblasting as a means of preparing steel surfaces for painting lies in the ready availability and relatively low cost of sand having a particle size conducive to production of an excellent anchor pattern on the cleaned surface.

6.3.1.8.1. *Sandblasting to "white" metal*, while not always feasible or economical, is the most thoroughly effective method available for preparing steel surfaces for painting. It removes all rust, mill scale, corrosive salts, dirt, grease, oil, wax, and other foreign matter from the metal—no matter how heavy the corrosion or contamination—leaving a completely clean uniform surface with an ideally roughened texture or profile (anchor pattern) for maximum coating adhesion and durability under the most severe service conditions. Although sandblasting is a relatively expensive method of surface preparation, the greater coating durability obtainable under adverse service conditions will often make it the most economical method in the long run. This is especially true in severe exposure environments, such as chemical atmospheres or water immersion. Thorough sandblasting is, in fact, the only method of surface preparation that will ensure maximum coating performance under such rigorous conditions.

There may be occasional situations, however, in which the pattern of corrosion would not justify complete sandblasting to white metal even for severe service exposure. For example, to remove the last traces of rust from a deeply pitted surface may be impractically expensive because of the extra labor involved and the excessive removal of sound metal required to reduce the entire surface to the level of the pits. In general, sandblasting can advantageously be employed wherever the greater coating durability obtainable by this method justifies the extra time and cost.

6.3.1.8.2. In less severe service environments, where maximum coating durability is not required, lesser degrees of sandblasting than cleaning to white metal are usually satisfactory. So-called *commercial blast cleaning* envisions a good but not perfect cleaning job in which nearly all rust, mill scale, and contaminants are removed from the surface, but not necessarily to the point where a surface of uniform color, texture, and cleanness is obtained. This degree of cleaning is significantly lower in cost than blast cleaning to white metal, and is generally adequate for all but the most rigorous types of service exposure.

6.3.1.8.3. To meet certain situations in corrosive environments where commercial blast cleaning is inadequate but white metal blast cleaning is prohibitively expensive, an intermediate grade called *"near-white" blast cleaning,* permitting a small specified amount of streaking and shadowing, has recently been established by the Steel Structures Painting Council [153] after successful use in industrial, state, and federal trials.

6.3.1.8.4. So-called *"brush-off" blast cleaning* is a rapid type of superficial sandblasting intended to remove all loose rust, loose mill scale, and loose paint from the surface, leaving only tightly adhering, intact mill scale and rust. This degree of surface preparation is comparable or superior to the best that can be accomplished by hand or power tool cleaning methods, and is adequate for coating systems with good wetting ability which are to withstand only mild exposure.

6.3.1.8.5. *Wet sandblasting* employs a slurry of sand and water instead of dry sand as the abrasive. Heavy rust and tight mill scale are effectively removed by this method, and the dust problems and hazards of dry sandblasting are largely eliminated. However, the clean, wet surface begins to rust again almost immediately unless corrosion inhibitors are incorporated in the blast water. Even when inhibitors are used, some doubt exists as to the efficacy of the passivated surface in promoting maximum adhesion and durability of the applied coating system. Wet sandblasting is not widely used now as a method of preparing steel surfaces for painting.

6.3.1.8.6. *Dry sandblasting equipment and techniques.*—An efficient sandblasting operation requires the right combination of nozzle type, hose size, abrasive size, air pressure and flow, and sand handling capacity—also, a competent nozzleman. Nozzles of widely different durability and cost may be made of ceramics, cast iron, steel alloys, tungsten-carbide, and other suitable materials. Nozzle size is limited by the requirement that the hose be 3 or 4 times larger in diameter than the nozzle and yet be reasonably flexible and manageable. For general sandblasting work, a $\frac{3}{8}$-inch nozzle, requiring a $1\frac{1}{4}$-inch hose, is the largest size that is practical. However, nozzles up to $\frac{5}{8}$-inch diameter can be used on large flat surfaces where their rigidity and unwieldiness do not seriously affect the overall production rate. A $\frac{3}{8}$-inch nozzle operated at an air pressure of 90 lb/in^2 requires about 210 ft^3/min of air and will pass about 1500 pounds of sand per hour. Both sand and air must be dry and oil-free. An optimum anchor pattern for painting is obtained with an abrasive size of 20 to 50-mesh. During blasting the nozzle is usually held at a slight angle from the perpendicular at a distance of 12 to 18 inches from the surface; however, an angle of about 45 degrees may be more effective for dislodging loose corrosion products or loose paint.

6.3.1.8.7. *Vacuum blast cleaning* systems are available for specialized use where dust is not permissible or when the abrasive is to be recovered. The blast nozzle is enclosed in a hollow cone having a brush at one end to trap the abrasive and cleaning debris while the vacuum exhaust is applied through the side of the cone.

6.3.1.8.8. *Cost and Production Rate.*—The overall cost per unit area of sandblast cleaning is determined primarily by the production rate, the cost of labor, and the cost of the abrasive. The production rate (surface area cleaned per unit time) will vary greatly with the nature and amount of corrosion products to be removed, with the degree of surface cleanness to be achieved, with the type of equipment and blasting conditions employed, and with the skill of the nozzleman. The available figures for production rates obtainable by the various degrees of sandblasting (viz, white metal, commercial, and brushoff) are not in good agreement; however, as a rough guide-line, under ordinary conditions, sandblasting to white metal may proceed at the rate of 50 to 150 square feet per hour, while the production rate for commercial blast cleaning may be about 3 times greater, and the production rate for brushoff

blast cleaning may be 6 to 8 times greater. Obviously, cleaning to white metal is considerably more expensive than commercial blast cleaning and is many times more costly than brushoff blast cleaning. The degree of cleaning to be done should be adequate for the particular coating system and service environment involved. Cleaning beyond this point is unnecessary and uneconomic, while less than the required degree of cleaning ultimately results in higher costs by shortening the service life of the coating.

6.3.1.8.9. *Safety.*—Sandblasting is a hazardous operation unless adequate precautions are taken to protect personnel and property against harm from dust and flying chips and particles. The nozzleman should be equipped with a U.S. Bureau of Mines approved helmet connected to a source of clean, compressed air. Other workers in the area should wear goggles and filter-type air respirators. Sandblasting is a constant menace to unprotected eyes, and inhalation of the dusts may cause silicosis. Blasting should not be done in areas where explosive concentrations of volatile vapors may be present. Blast hoses should be grounded to dissipate static charges. Nearby property should be protected by covering, masking, or wrapping. Ropes used for scaffolding should be heavily wrapped to prevent damage. Wet sandblasting, while free of dust hazards, presents a hazard from the toxic, soluble chromium compounds (corrosion inhibiting agents) contained in the mist. For detailed information on safe practice in sandblasting, reference may be made to the codes or manuals of various national associations concerned with this problem [75,76,77].

6.3.1.8.10. *After sandblasting* is completed, any traces of residual dust, debris, or abrasive should be completely removed by brushing with clean brushes, blowing with clean compressed air, or vacuuming. The fresh, sandblasted, bare metal surface is very susceptible to corrosion and will rust quickly if wet or exposed to high humidity. The clean surface must be treated or primed promptly, before rusting or contamination can occur. Even in ordinary mild atmospheres, it is highly desirable that the surface be primed or chemically treated within eight hours after sandblasting.

6.3.1.9. FLAME CLEANING, depending on the manner in which it is employed, can be used either to remove all *loose* mill scale and rust from unpainted steel or to remove old paint from metal surfaces. For the removal of mill scale and rust from unpainted steel, an intensely hot, high-velocity, oxy-acetylene flame is passed over the metal surface at the rate of about 15 to 35 feet per minute. The rapid heating and differential expansion of the mill scale and base metal, aided by the "explosive" action of water vapor generated beneath the scale, breaks it loose from the surface so that it can be removed by scraping and wire brushing. Rust is converted to a black powder that may then be brushed from the surface. Heavily rusted and heavily scaled steel may require a slow traverse or several passes of the flame to accomplish the removal. Tightly bonded mill scale is not removed by flame cleaning.

Immediately following the flame treatment, the surface should be power wire brushed or scraped to remove all loosened rust, scale, and foreign matter, and then swept or brushed free of any residual dust and debris. Promptly after the flame treatment and cleaning—while the metal is still warm and well above the temperature of the surrounding atmosphere—the prime coat should be applied. Unless the prime coat is applied promptly to the warm metal, before any moisture becomes absorbed on the surface, most of the benefits of the flame cleaning will be lost and the results will be little if any better than power tool cleaning alone. The requirement that priming follow so closely upon the heels of the flame cleaning and wire brushing creates both scheduling problems and a possible fire hazard, since the primers employed usually contain volatile, flammable solvents. The priming must be conducted in a manner that will not result in the buildup of explosive concentrations of solvent vapor in the area of the flame.

If oil or grease are present on the surface, they should be removed by solvent cleaning—and the solvent allowed to evaporate—before using the flame cleaning method. Grease and oil may char under the rapidly moving flame, leaving an objectionable carbon deposit on the surface.

When properly done, flame cleaning is considered to give results better than that obtainable by power tool cleaning alone, but it is not a substitute for sandblasting to a "commercial" surface or to "white" metal.

Flame cleaning is very useful in maintenance painting where it is necessary to remove all the old paint from the metal. For this purpose, slow traverse of the flame head and multiple passes are usually required. While the usual oxy-acetylene flame cleaning equipment is suitable, other types of torches utilizing propane, gasoline, or other fuels capable of hot flame may be used. Coatings that soften with heat can be removed with a scraper immediately following the flame. For coatings that are not softened appreciably by heat, the flame must be held at one place until the coating is burned away, after which the ash and any carbonaceous residue must be removed by scraping or wire brushing. The considerable labor involved in the removal of such residues can be reduced

by the use of special flame cleaning equipment in which the oxy-acetylene flame is supplemented by a jet of oxygen which assists the burning and at the same time blows the residue from the surface as it forms.

6.3.2 Chemical Pretreatment of Steel (and Iron) Surfaces

As indicated previously, metal surfaces are given chemical pretreatments to form a corrosion-inhibiting, paint-receptive coating on the surface through a chemical reaction with the metal. In practice, such conversion coatings for steel and iron are nearly always insoluble metal phosphates, although chromate and oxide coatings find limited application. Phosphate coatings, though insoluble in water, are capable of absorbing small amounts of corrosion inhibitors (notably, chromic acid) from dilute solution to enhance corrosion resistance and further increase the life of the applied paint. It is for this reason that most phosphatizing processes specify a final rinse in dilute chromic acid or a dilute chromic-phosphoric acid mixture.

In addition to the direct phosphating types of inorganic pretreatment, wide and effective use is made of the wash primer or washcoat type of organic pretreatment coating. The latter provides a mild phosphatizing action on the surface while laying down a thin, very adherent organic film. Organic pretreatment coatings should not be used over surfaces that have already received a phosphate pretreatment.

The chief types of inorganic phosphate pretreatment and the organic coating (wash primer) type of pretreatment are described in the following subsections.

6.3.2.1. COLD PHOSPHATE PRETREATMENT (PHOSPHORIC ACID TYPE): This type of pretreatment utilizes relatively dilute phosphoric acid solutions to etch the surface lightly and convert a very thin layer of the metal to an insoluble phosphate coating weighing about 8 milligrams per square foot of surface. The solutions employed are similar to those used in the phosphoric acid cleaning of metals as described in section 6.3.1.5.1; however, when these materials are used as a pretreatment, the emphasis is upon chemical conversion of the metal rather than on cleaning. The surface should previously have been cleaned free of all oil, grease, dirt, mill scale, and rust—except for very light rust which may be converted during the treatment. If used over mill scale, the scale may later loosen and lift the paint. Unlike acid cleaning processes in which the solutions may be used hot and profusely and for relatively long periods of time, the technique in pretreating is to apply only the necessary amount of conditioner and to leave it on only for a brief period—until the acid has reacted

with the metal to form the desired gray-white phosphate coating—before washing or wiping off the excess acid and any loose residue.

Suitable cold phosphating solutions containing phosphoric acid, an oil solvent, a wetting agent, and water are described in Military Specification MIL–M–10578 [78]. This specification covers two types of metal conditioning compounds, both of which must be diluted with three times their volume of water before use. The two types differ primarily in phosphoric acid concentration. Type I, after dilution for use, contains about 10 percent by weight of phosphoric acid; type II contains about 3 percent by weight of phosphoric acid after dilution.

The stronger, type I solution is used where some light rust is present and where the surface can be washed off to remove all reacted phosphoric acid. Free phosphoric acid on the surface is detrimental to paint life. After the treated surface has been thoroughly washed, it should be given a final rinse with a dilute chromic acid or dilute chromic-phosphoric acid mixture to passivate the surface. A chromic acid concentration of about 0.02 to 0.05 percent by weight is satisfactory.

The weaker, type II conditioner is used where it is not practicable to rinse off the treated surface. The conditioner, after proper dilution (with three times its volume of water, or more if necessary), should be applied sparingly to the clean metal surface and allowed to react with the surface and dry upon it to form a grayish-white deposit of insoluble phosphate. If the proper strength and amount of solution are used, all the phosphoric acid will be reacted and it will not be necessary to wipe off or further treat the surface. However, if any unreacted phosphoric acid remains on the surface (as evidenced by a dark, sticky residue), it must be wiped off with damp rags or with rags wet with an alcohol-water mixture to remove all traces of stickiness, and the surface again allowed to dry. The dried surface should have a white appearance; however, any excessive or loose powdery deposit should be brushed off with dry brushes or dry rags, or removed with clean compressed air or by vacuuming.

The treated surface should be given a priming coat of paint as soon as practicable, before any rusting or contamination of the surface occurs.

Cold phosphate pretreaments are not intended for use in maintenance painting where the acids employed may contact and damage existing paint. The solutions should not be stored or mixed in uncoated steel or galvanized steel containers; glass or earthenware vessels are satisfactory.

Precautions are necessary to protect workmen from accidental splashes of the acid solutions. The solutions are particularly danger-

ous to the eyes; splashproof eye shields or goggles should be worn to prevent painful, serious injury. Acid-resistant rubber gloves, aprons, and boots should be provided where needed.

6.3.2.2. COLD PHOSPHATE PRETREATMENT (ZINC PHOSPHATE TYPE): Proprietary zinc phosphatizing solutions containing zinc phosphate, phosphoric acid, and an activating agent are available which can be applied unheated to steel or galvanized surfaces, using ordinary application methods such as brush, spray, dip, or flow coating. The surface to be treated should first be cleaned by an appropriate method (see sec. 6.3.1) to remove any oil, grease, dirt, rust, and mill scale. The dilute, unheated phosphatizing solution is then applied in accordance with the manufacturer's instructions and allowed to remain on the surface until the zinc phosphate coating is formed (usually for two to five minutes). The surface is then thoroughly washed with clean water. A final rinse in dilute chromic acid or a dilute chromic-phosphoric acid mixture is usually specified in order to achieve maximum corrosion resistance and paint life. The priming paint should be applied to the phosphated surface as soon as practicable after it is dry.

6.3.2.3. HOT PHOSPHATE PRETREATMENT (ZINC PHOSPHATE TYPE): These are proprietary processes based on specially formulated, balanced solutions of phosphoric acid saturated or supersaturated with acid zinc phosphate salts (plus accelerating agents) that deposit a heavy, visibly crystalline coating of zinc phosphate (weighing about 150 to 400 milligrams per square foot) on the surface of the metal. By providing substantial protection against the spread of corrosion beneath the paint film as well as a physically receptive surface for excellent paint adhesion, the heavy phosphate coating significantly increases the durability of the applied paint, particularly under severe service conditions involving corrosive atmospheres or water immersion. (For mild exposure conditions, where it is neither economic nor necessary to thoroughly clean the metal surface by sandblasting, the benefits of hot phosphatizing may not be sufficient to justify the additional cost of such treatment.) Hot zinc phosphate pretreatments are largely limited to objects of a size and shape that can be treated in dip tanks or by spraying in appropriate enclosures. They are therefore particularly suitable for the pretreatment of fabricated steel on the production line. There have been some developments in special thioxotropic or gelled phosphate solutions for field application, but these have not been widely used. Hot phosphate treatments are not used in maintenance painting.

Hot phosphate pretreatments require a completely clean bare surface, preferably one that has been sandblasted if heavy rust or mill scale was present. In any event, the surface should be free of oil, grease, dirt, paint, rust, and mill scale. Federal Specification TT–C–490 [79] specifies that the clean metal should be exposed to the hot phosphating solution for at least three minutes if a dip method is used or for at least 1 minute if spraying is employed. The equipment used should be constructed of materials resistant to the action of the phosphating solution and should not contain copper alloy fittings or brazing where they may come in contact with the solution. Fog sprays should be provided on both dip tanks and spray equipment to prevent the solution from drying on the work surface before the necessary subsequent washing with water. Hot phosphate residues are detrimental to paint life and must be removed by thorough washing with hot or cold clean water, followed by a final rinse with a dilute chromic acid or chromic-phosphoric acid mixture to enhance corrosion resistance and paint life. The work should remain in the chromic rinse for a minimum of 1 minute when dipped or for at least 30 seconds in spray processes. TT–C–490 specifies that the chromic acid rinse solution be maintained at a temperature of 140 to 210 °F (60 to 99 °C) and a pH of 2 to 4. Industry recommendations do not necessarily coincide with those given in TT–C–490, and the instructions of the manufacturer or supplier should be consulted in the case of specific proprietary materials. Industry recommendations frequently call for lower temperatures (room temperature to about 160 °F [71 °C]) and a higher, more stringently controlled pH (4 to 5) than those given in TT–C–490.

The zinc phosphate coating should be continuous, uniform in texture, evenly deposited, and gray to black in color. It should not be mottled in appearance nor show any smut, powder, corrosion products, or white stains from dried phosphating solutions. Light brown or orange stains from the chromic acid rinse do no harm; however, deep brown stains may be evidence of heavy concentrations of chromic acid which might cause blistering of some paint films. The minimum weight of the phosphate coating should be 150 milligrams per square foot for spray processes and 300 milligrams per square foot for dip processes.

Care should be taken to prevent burns from the hot solutions or toxic effects from the chromic acid rinse. Splash-proof eye shields should be worn to avoid painful damage to the eyes.

The phosphated surface should receive a priming coat of paint as soon as practicable, before any contamination or deterioration of the surface occurs.

6.3.2.4. HOT PHOSPHATE PRETREATMENT (IRON PHOSPHATE TYPE): These are proprietary processes based on balanced aqueous solutions of phosphoric acid and acid phosphate salts, with or without accelerating agents, which build up a coating of insoluble amorphous iron phosphate on the surface of the metal. The iron phosphate coatings thus obtained are not as heavy as those yielded by the hot zinc phosphate processes. A minimum coating weight of 40 milligrams per square foot is usually specified, and the coating weight that can be built up usually does not exceed 100 milligrams per square foot. The thinner, amorphous coating of iron phosphate is more flexible than the crystalline zinc phosphate type and hence is preferred in applications where the metal is to be formed after painting. Like zinc phosphate coatings, the iron phosphate coatings provide substantial protection against the spread of corrosion beneath the paint film as well as a physically receptive surface for excellent paint adhesion, thus contributing significally to increased paint life, especially under severe service conditions such as corrosive atmospheres or water immersion.

Hot iron phosphate pretreatments are limited to objects of a size and shape that can be treated in dip tanks or in specially designed spray enclosures. They are particularly suitable for the factory pretreatment of production line items. As with other hot phosphate pretreatments, the surface to be treated must be completely clean—free of oil, grease, dirt, paint, rust, and mill scale. The treatment should be continued until a phosphate coating is produced which is insoluble in water and has a color ranging from a golden yellow to purple. Federal Specification TT–C–490 [79] specifies that the items be exposed to the phosphating solution for at least three minutes in dip processes or for at least 1 minute in spray processes. The article should then be rinsed in clean water, followed by a final rinse with a dilute chromic acid (or dilute chromic-phosphoric acid) solution similar to that used in zinc phosphate processes (see sec. 6.3.2.3). The hot phosphate residues are detrimental to paint life and should not be allowed to dry upon the surface prior to removal by washing.

The insoluble, golden yellow to purple iron phosphate coating should be continuous, uniform in texture, and evenly deposited. There should be no smut, power, corrosion products, or white stains due to dried phosphating solutions on the surface.

Precautions should be taken to prevent burns from the hot solutions or toxic effects from the chromic acid rinse. Splashproof eyeshields should be worn to prevent painful, serious damage to the eyes.

The phosphated surface should receive a coat of priming paint as soon as practicable, before any contamination or deterioration of the surface occurs.

6.3.2.5. ORGANIC PRETREATMENT COATING (WASH PRIMER): The wash primer or wash coat type of pretreatment provides a mild phosphatizing action on the metal surface while laying down a thin, highly adherent organic film which provides an excellent base for most organic coating systems. The wash primer type of pretreatment is particularly useful where the size and shape of the work preclude the use of hot phosphate solutions or where mixed metal assemblies are to be treated. The wash primer pretreatment is of maximum effectiveness and outstanding benefit when used on thoroughly cleaned steel (sandblasted or pickled) which will be exposed to severely corrosive atmospheric conditions or to water immersion. It also improves the durability of conventional paints on hand cleaned steel exposed to corrosive atmospheres or water immersion. For hand-cleaned steel to be exposed in mild, ordinary atmospheres, the wash primer pretreatment—while beneficial—may not be economically justifiable. Wash primer should not be used on phosphated steel or over other pretreatments.

6.3.2.5.1. Two-component wash primer.— The most widely used and proven type of wash primer organic pretreatment coating is the two-component type comprising (1) a base material containing an alcohol solution of polyvinyl butyral resin pigmented with insoluble basic zinc chromate, and (2) an activating diluent in the form of an alcohol solution of phosphoric acid. This is the type of pretreatment commonly known as WP–1, or as Bureau of Ships Formula No. 117 as covered by Military Specification MIL–C–15328 [30]. A similar composition providing a smoother finish for aircraft use is covered by MIL–C–8514(Aer) [80]. Application methods for this type of pretreatment are given in MIL–C–8507 [81].

The resin base and the acid diluent must be mixed just before use and should be applied within 4 hours after mixing. The fresher the mixture, the better are the results obtained. Since the phosphoric acid reacts with the vinyl resin and the pigment, as well as with the metal surface, the activated mixture may gel, or, in any event, become useless for its chief function of promoting good adhesion if it stands for more than about 8 hours. It is essential that the base material be thoroughly mixed by vigorous mechanical shaking or stirring to reincorporate all settled pigment or caked material before adding the activating diluent (the latter also should be shaken before use).

For use, one part by volume of the phosphoric acid activator-diluent should be added *slowly, with continuous stirring* to prevent localized

gelling, to four parts of the resin base. *The resin base should never be added to the diluent.* The activated mixture should be thinned to spraying consistency with alcohol; generally, a volume of thinner equal to that of the added diluent will suffice, but up to double this volume is permissible if necessary to obtain a thin, *wet*, uniform film. The added alcohol should normally be either ethyl alcohol or isopropyl alcohol; however, under high humidity conditions, some butyl alcohol may be substituted for a portion of the lower boiling alcohols to an extent sufficient to prevent blushing. The dry film thickness should be 0.2 to 0.3 mil for optimum results and should not exceed 0.5 mil in any case. At the correct thickness, the film will have a greenish-yellow translucent appearance through which uneven coloring in the substrate will show. Wash primer should never be applied so thick as to hide the substrate. It should be emphasized that the washcoat must be laid down wet to obtain a continuous film; otherwise, the coating will be powdery and its adhesion seriously impaired.

Brush application, while generally less satisfactory than spray, may be used on rough surfaces or for touching up small areas. When spot treating previously painted surfaces, the wash primer should ordinarily be applied only to bare areas, although overlap of the surrounding paint is not harmful provided the washcoat adheres well to the old paint and does not lift it.

The wash primer pretreatment should not be thought of as a coat of paint. While it may afford temporary protection for several weeks under mild, dry conditions (more than is afforded by an inorganic phosphate coating), it is not intended for use as a shop coat or to protect against exposure. For optimum adhesion and best results, the wash primer should receive a coat of priming paint as soon as it is completely dry—usually in from one to four hours after the pretreatment. Intercoat adhesion will be impaired either by premature application of the primer or by unnecessarily long aging of the washcoat. Virtually any type of primer and many types of coatings can be used over the wash primer pretreatment with good results; certain lacquers and vinyl paints are among the exceptions that require special primers or intermediate coats.

6.3.2.5.2. *Single-package wash primers* based on lead chromate pigment or on chromic-phosphate pigments have recently become available. A wash primer of this type for use on steel, aluminum, and magnesium is covered by Federal Specification MIL–P–14504 [82]. These are proprietary materials, and the directions of the manufacturer should be followed in their use. While the convenience of a single-package wash primer is obvious, these materials do not yet have the long history of successful use that is enjoyed by the two-component wash primers, and the one-package wash primers have not found wide use.

6.3.3. Galvanized Surfaces

Serious difficulty has often been experienced in obtaining good adhesion of conventional paints to galvanized steel, especially to new galvanized surfaces. All too often, the paint peels or flakes off after a short period of exposure. A chief cause of such early adhesional failure, apart from improper cleaning of the surface, is thought to be the reactivity of new zinc with many paint vehicles. While the nature or mechanism of this reaction is not well understood, practical means for dealing with the problem are available. Good adhesion and durability of paints applied on galvanized surfaces can be ensured by: (1) thorough cleaning of the surface, and (2) adequate weathering and/or chemical pretreatment of the surface to form a paint-receptive barrier layer that insulates the paint film from the reactive zinc while shielding the zinc from further attack by atmospheric corrosive agents.

6.3.3.1. NEW GALVANIZED SURFACES frequently are coated with factory processing compounds, temporary protective oils, and other contaminants harmful to paint adhesion unless removed prior to pretreatment or painting. In addition, most of the galvanized sheet and strip made today is given a chromate treatment of one kind or another at the mill to protect against white stain, particularly if the metal is destined for warehouse storage. Surfaces thus treated may not be receptive to some types of paints and cannot be further pretreated by the methods usually prescribed for galvanized steel. Where it is desired to use a particular pretreatment (e.g., hot phosphating) on galvanized steel, the problem is best avoided by specifying "no treatment" on the mill order. When the metal is obtained from a warehouse and the nature of the factory treatment is unknown, probably the best practice is to solvent-clean the surface (using a spectrum of solvents if necessary) and then apply a zinc dust primer such as that covered by Fed. Spec. TT–P–641 [29], followed by the desired finish. The problem has been considered by the American Iron and Steel Institute [83] and by the American Society for Testing and Materials [84].

Zinc dust primers generally give good results on clean galvanized surfaces with or without pretreatment. However, pretreatment is beneficial and is recommended where the maximum possible service life is sought, provided that the galvanized surface has not previously been given an interfering factory chromate treatment.

For optimum results, new galvanized surfaces should be thoroughly solvent-cleaned by one of the methods described in section 6.3.1.1 to produce a surface completely free of oil, grease, processing compounds, temporary protective substances and other foreign matter. The clean surface, if not factory chromated as noted above, should then be given one of the following pretreatments:

(1) Hot zinc phosphate pretreatment similar to that described in section 6.3.2.3 but specially formulated for galvanized surfaces, provided that the item is of a size and shape that can be treated in hot dip tanks or in special spray enclosures. A pretreatment of this type is covered by specification MIL–T–12879, Type I, Class 1 [85].

(2) Cold zinc phosphate pretreatment of the brush-on or wash type described in section 6.3.2.2.

(3) Wash primer type of organic pretreatment coating as described in section 6.3.2.5.

(4) Cold phosphate pretreatment of the dilute phosphoric acid type as described in section 6.3.2.1.

(5) Chromate pretreatment of the general nature described in section 6.3.6.1 and as covered by specification MIL–T–12879, Type I, Class 2 [85].

The best choice among the above recommended pretreatments is largely a matter of convenience as determined by the size and shape of the object, its location, and the application equipment and facilities available. The most generally applicable and most widely used pretreatment is the wash primer type; it gives excellent results in virtually all situations. The proprietary zinc phosphate pretreatments, either hot or cold, also give excellent results; where the hot zinc phosphate pretreatment is feasible—as in factory coating operations—it is probably the best pretreatment available. The dilute phosphoric acid type of cold phosphate pretreatment, while less effective than the others, may be the expedient choice in situations where the treated surface cannot be rinsed off or where other application limitations exist.

Chromate treatments are more often used for the protection of zinc surfaces against white stain rather than as a paint base; to ensure the paintability of a chromate-treated surface, it is essential that a prepaint type of treatment be specified [85].

"Home cure" treatments such as washing the galvanized surface with vinegar, cider, acetic acid, muriatic (hydrochloric) acid, or copper sulfate solution have been shown to be useless or even harmful and should be avoided.

6.3.3.2. OLD GALVANIZED SURFACES that have weathered for six months or more—so that oils,

processing compounds, and protective treatments (including factory chromate treatments) —have been largely removed from the surface may frequently be painted satisfactorily with conventional paint systems provided the surface is first cleaned with solvent to remove any residual oil or soil. For reliable results, however, chemical pretreatment (if no residual chromate coating is present) and/or the use of zinc dust primer is highly recommended. If the surface is too soiled for adequate cleaning with solvents alone, it may be brushed lightly with steel wool to assist in removal of the soil and then brushed, blown, vacuumed, or again solvent washed. Rusted areas on galvanized steel should be hand cleaned or wire brushed in the same manner as rusty steel. If large areas of the galvanized surface are badly rusted, it will be necessary to clean the entire surface by the same vigorous methods (e.g., acid cleaning or sandblasting) that are used for rusted steel (see sec. 6.3.1).

6.3.3.3. CADMIUM SURFACES may be cleaned, pretreated, and successfully painted by the same methods that are employed for galvanized (zinc-coated) surfaces (also see sec. 6.3.6.2).

6.3.4. Aluminum and its Alloys

Aluminum and its alloys should be solvent-cleaned by one of the methods discussed in section 6.3.1.1 to remove all oil, grease, soil, and other foreign matter. The use of mechanical cleaning methods is damaging to the surface, particularly where a thin cladding of aluminum is present on a substrate of a harder alloy. Where the surface is too soiled or deteriorated to be adequately cleaned with solvents alone, the minimum amount of brushing with stiff bristle or aluminum wool that will dislodge the soil should be used.* All debris from the mechanical cleaning operations should be swept from the surface or removed with clean, compressed air or by vacuuming, and any residual oily contaminants should be removed by another solvent wash.

The clean surface should be pretreated immediately by one of the following methods:

(1) Wash primer type of organic coating pretreatment described in section 6.3.2.5 and covered by MIL–C–15328 [30].

(2) Chemical coating pretreatment covered by Military Specification MIL–C–5541 [86].

(3) Anodic coating pretreatment by the chromic acid process or the sulfuric acid process, both of which are covered by MIL–A–8625 as Type I and Type II, respectively [87].

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*Steel wool or wire brushing should be avoided, since it may result in the embedment of fine steel particles in the soft aluminum surface that are difficult to dislodge and may cause serious galvanic rusting and pitting.

Of the above methods of pretreatment, the wash primer type is best suited for use in the field. It gives excellent results and is widely used in both field and industrial applications. For best results, the wash primer should receive a coat of priming paint within about 1 to 4 hours—after it is adequately dry but before it ages unnecessarily. A zinc yellow primer such as that covered by Fed. Spec. TT–P–666 [88] is highly recommended for use over the wash primer on aluminum surfaces. Other primers in which zinc yellow constitutes a major portion of the pigment, such as that covered by TT–P–645 [89], may also be used.

The chemical "films" covered by MIL–C–5541 are intended to be chemical pretreatment coatings designed to improve paint adhesion and to inhibit underfilm corrosion. Products meeting these requirements[1] usually produce a chromate-type coating on the surface of the aluminum, either by chemical reaction with the surface or by deposition of the coating from solution or by a combination of the two processes. Despite the wide and effective use of these chromate-type coatings, their exact chemical composition is not reliably established. They have been variously described as chromium chromates, chromate-chromic oxides, and chrome-aluminum oxide complexes; however, all of them are derived from acidic hexavalent chromium solutions of the general nature described in section 6.3.6.1, and they all produce thin amorphous corrosion-inhibiting films having excellent paint-base qualities on aluminum surfaces. In an older, less widely used industrial pretreatment process, coatings consisting essentially of zinc and aluminum phosphates are formed on the aluminum surface by treating it with zinc phosphate solutions containing fluoboric acid; these are crystalline phosphate coatings similar to those formed on steel or zinc by other proprietary processes (see secs. 6.3.2.2 and 6.3.2.3). While many of the chemical pretreatments which have been mentioned are designed for industrial use, others may be used in the field; the instructions of the manufacturer should be followed in their selection and use.

The anodic coating type of pretreatment (covered by MIL–A–8625), using chromic acid or sulfuric acid as the electrolyte in an anodizing bath, is limited to industrial applications. The oxide coatings produced by anodic treatments are denser and less porous than most chemical conversion coatings, but they may still be improved by sealing with a hot water treatment containing dilute amounts of chromate or dichromate salts.

¹ See Qualified Products List QPL-5541 established for Military Specification MIL-C-5541 by the Bureau of Naval Weapons, Department of the Navy, copies of which can be obtained by writing the Commanding Officer, Naval Supply Depot, 5801 Tabor Avenue, Philadelphia, Pennsylvania 19120.

6.3.5. Magnesium and its Alloys

The corrosion resistance and the paintability of magnesium and magnesium-base alloys can be greatly increased by application of a suitable chemical or electrochemical pretreatment prior to application of a suitable primer. (Primers for use on magnesium surfaces are usually of the zinc chromate type. They must be carefully selected to provide adequate adhesion (see sec. 2.4.2.4)). Most of the paint-base treatments are of the chromate type. Before chemical pretreatment, the magnesium surface should be thoroughly cleaned to remove all oil, grease, welding flux, soil, oxides, or other foreign matter.

6.3.5.1. CLEANING.—Since magnesium, unlike aluminum, is not attacked by caustic solutions, highly alkaline cleaners similar to those used for the heavy duty cleaning of steel (see sec. 6.3.1.4) may be employed, and this is the preferred method for cleaning ordinary grease and soil from magnesium-base surfaces. The alkaline cleaner should be maintained at a pH above 11 for general cleaning and at a pH above 13 for the removal of graphite lubricants; the latter is accomplished by soaking the part for 10-20 minutes in the hot caustic (about 200 °F [93 °C]), followed by thorough rinsing in cold water and immersion in a chromic-nitrate pickle to complete removal of burned-on lubricant. Old paint coatings may be removed with alkali paint removers such as that covered by Federal Specification TT–R–230 (see summary chart in sec. 8.2).

6.3.5.1.1. *Electrochemical cleaning* considerably shortens the cleaning time. Using an alkaline cleaning bath at a temperature of about 200 °F (93 °C) and a pH above 11, the parts are made cathodes in the bath employing a current density of 10 to 40 amperes per square foot at 6 volts for 3 to 10 minutes.

6.3.5.1.2. *Alkaline cleaning of any type must always be followed by thorough rinsing in cold water.* Alkaline residues are very detrimental to paint life. Even when acid pickling is to be used subsequent to alkaline cleaning, it is essential to rinse away all alkaline or soapy residues, since soaps carried over into the acid bath will form an oily layer on the surface of the liquid which will contaminate the work as it is immersed or withdrawn.

Where large amounts of oily or greasy contaminants are present on the magnesium surface, they should be removed by solvent cleaning (see sec. 6.3.1.1) prior to alkaline cleaning to avoid premature fouling of the alkaline cleaner.

6.3.5.1.3. *Acid pickling* is used to remove oxide layers, old chemical finishes, burned-on drawing and forming lubricants, and other water-insoluble or non-emulsifiable substances from magnesium-base surfaces. Chromic acid pickling is preferred for general cleaning and for the removal of surface oxidation and corrosion products; this type of pickle does not result in dimensional loss and may be used on parts with tolerance limits. A chromic-nitrate pickle is used primarily for the removal of burned-on graphite lubricants. Sulfuric acid pickling is used on magnesium sand castings to remove the effects of blasting operations; alternatively, a nitric-sulfuric acid pickle may be used for this purpose. A chromic-nitric-hydrofluoric acid pickle may be used for the pickling of castings, particularly die castings. A strong phosphoric acid pickle also may be used for cleaning all types of die castings. For the removal of mill scale, particularly from sheet material, and to ensure maximum corrosion protection, an acetic-nitrate pickle is employed; this pickle normally removes from 0.0005 to 0.001 inch of metal from the surface. *Acid cleaning must always be followed by thorough rinsing in cold running water.*

Further details about the aforementioned acid pickling and alkaline cleaning materials are given in Military Specification MIL–C–3171 [90]; this specification also describes methods for the chemical pretreatment of magnesium surfaces. Useful information on the cleaning and pretreatment of magnesium surfaces may also be found in the publication "Magnesium Finishing" [90a] and in the Metal Finishing Guidebook [91].

6.3.5.1.4. *Mechanical cleaning methods* (see secs. 6.3.1.6, 6.3.1.7, and 6.3.1.8), including sanding, grinding, wire brushing, and grit-, shot-, or sand-blasting, may be used on rough unmachined castings that are discolored or corroded. Blasting methods may result in surface contamination which will greatly increase the initial corrosion rate of magnesium. Hence, blast cleaning should always be followed by pickling in a sulfuric acid or sulfuric-nitric acid pickle until 0.002 inch of surface has been etched away.

6.3.5.2. CHEMICAL PRETREATMENTS for increasing the corrosion resistance of magnesium alloys and for producing a paint-receptive surface are covered in detail in Military Specification MIL–M–3171 [90] and elsewhere [90a, 91]. Since virtually all the processes now in use for the pretreatment of magnesium surfaces (except the HAE process) were developed by a single manufacturer [90a], these processes have been identified for the sake of clarity by their commonly known proprietary

designations in the discussion which follows. Before application of chemical treatments, the surface should be thoroughly cleaned by the methods indicated in the preceding section. Five types of chemical pretreatment are described in MIL–M–3171; these are summarized below:

6.3.5.2.1. *Type I Chrome-Pickle Treatment* (Dow No. 1) is of general applicability and is the most widely used chemical treatment for magnesium surfaces. In addition to providing a suitable base for paint, it is used for the temporary protection of parts during storage and shipment, and for touching up previously treated work. The treatment is applicable to all magnesium alloys (including those containing steel or brass inserts) when close tolerances are not required; the treatment removes about 0.0006 inch from the surface of the metal. The treatment utilizes a sodium dichromate-nitric acid solution for wrought magnesium, with the addition of a small amount of sodium, potassium, or ammonium acid fluoride to the bath for treating molded or cast magnesium. Dipping is the preferred method of application, but brushing may be employed on work too large for immersion. Close control of immersion time (normally 30 seconds to 2 minutes) in relation to bath composition is essential. After immersion, the part should be allowed to drain for a few seconds before being washed thoroughly in cold running water followed by a hot water dip to facilitate drying. In brush application, fresh solution should be generously applied and remain on the surface for at least one minute before being thoroughly washed off with cold running water. Excessive immersion, or failure to keep the surface wet with solution during brush application, will produce a powdery coating that is unsatisfactory as a paint base. When properly applied, the Type I treatment produces a matte gray to yellow-red, iridescent coating that exhibits a pebbled etch finish under magnification. A bright, brassy, relatively smooth surface (the result of excessive nitric acid or nitrate salt build-up in the bath) is not suitable as a base for paint, although it is satisfactory for the protection of parts during shipping and storage.

6.3.5.2.2. *Type II Sealed Chrome-Pickle Treatment* (Dow No. 10), while less often specified than Type III, may be used for the general long term protection of all magnesium-base alloys when close dimensional tolerances are not required. It provides a good paint base in addition to its protective qualities. While most commonly used for wrought products, it may also be used on castings. The treatment is a combination of chrome pickle and dichromate boil. The chrome pickle treatment is

applied as described under Type I, except that the parts need not be dried after rinsing. The freshly chrome pickled parts are then immersed for 30 minutes in a bath of boiling sodium dichromate solution saturated with calcium or magnesium fluoride and maintained at a pH of 4.0 to 5.5. After the immersion, the parts should be thoroughly rinsed in cold running water, followed by a hot water dip to facilitate drying. (The dichromate treatment must not be applied to old chrome pickled surfaces; the old chrome pickle film should have been removed by chromic acid pickling and/or heavy duty alkaline cleaners as described under Cleaning in sec. 6.3.5.1). The coating produced has the brown color of the dichromate superposed on the varying matte gray to yellow-red iridescence of the chrome pickle.

6.3.5.2.3. *Type III Dichromate Treatment* (Dow No. 7) is suitable for the long term protection of all magnesium-base alloys except those containing manganese or cerium, including work for which close dimensional tolerances are required. It provides a very good combination of paint base and protective qualities. The treatment does not appreciably affect dimensions and normally is applied after machining. Parts containing bearings and inserts of brass, bronze, cadmium plate, and steel are not affected by the treatment, but aluminum is rapidly attacked during the hydrofluoric acid dip which is an important step in this treatment. Where aluminum inserts or rivets are used, an acid fluoride dip is employed instead of the hydrofluoric acid dip. The hydrofluoric acid or acid fluoride dip both cleans and activates the magnesium surface (however, the surface should have previously been cleaned by the methods indicated in sec. 6.3.5.1). The hydrofluoric acid bath must be maintained between 10 and 20 percent HF; if allowed to become weaker than 10 percent HF, the magnesium will be severely attacked. It is recommended that wrought alloy containing 3 percent aluminum and 1 percent zince be immersed for 30 seconds and that all other wrought alloys and castings be immersed for 5 minutes at a temperature of 70-90 °F (21-32 °C). After immersion, the parts should be thoroughly rinsed in cold running water to minimize fluoride carry-over into the dichromate bath which would render it inoperative. After the fluoride treatment, the parts are immersed for 30 minutes in a boiling sodium dichromate solution saturated with calcium or magnesium fluoride and maintained at a pH of 4.0 to 5.5 (as described for the type II treatment). Properly applied coatings vary from light to dark brown depending on the alloy. After the dichromate treatment, the parts should be given a thorough rinsing in cold running water, followed by a hot water dip to facilitate drying.

6.3.5.2.4. *Type IV Galvanic Anodizing Treatment* (Dow No. 9) may be applied to all magnesium-base alloys for long term protection and to provide a good base for painting. The treatment causes no dimensional change and may be applied after machining operations. The parts are first cleaned as indicated in section 6.3.5.1 and then given the hydrofluoric acid or acid fluoride dip specified in the type III treatment. The work is then galvanically anodized for 10 to 30 minutes in a solution containing 4 oz. of ammonium sulfate, 4 oz. of sodium dichromate, and 1/3 fl. oz. of ammonium hydroxide per gallon of solution. The pH of the bath is maintained between 5.3 and 6.0 by additions of a chromic-sulfuric acid solution containing 5 percent by weight of each. The anodizing is carried out at a bath temperature of 120-140 °F (49-60 °C) and a current density of 2-10 amperes per square foot. The tank, if steel, is made the cathode; if the tank is nonmetallic, steel cathode plates must be provided. The work is electrically connected to the cathode through an external circuit that includes an ammeter and rheostat; the work must not be allowed to contact the cathode directly. Ordinarily, 70 to 150 ampere-minutes per square foot of work is sufficient to produce a uniform coating. A properly applied type IV coating is usually uniformly black or dark brown in color. Gray and nonuniform coatings indicate that articles were not properly cleaned before treatment or that the anodizing solution was depleted. After immersion, the parts should be thoroughly rinsed in cold running water, followed by a hot water dip or exposure to heated air to facilitate drying. The specified paint coating (usually a zinc chromate primer) should be applied as soon as practicable after the treated parts are thoroughly dry.

6.3.5.2.5. *Type V Caustic Anodizing Treatment,* while of some benefit for the protection of magnesium-base alloys, is no longer recommended because of the availability of newer and more satisfactory anodic treatments, such as those described in the following section.

6.3.5.3. ANODIC OR ELECTROCHEMICAL TREATMENTS are generally considered to provide the maximum in corrosion resistance and paint adhesion. Hard coatings with good abrasion resistance also can be obtained. Anodic processes produce relatively thick, dense, adherent protective coatings on magnesium alloys. It is essential that the work be clean and that good electrical contacts be established to ensure a uniform coating.

6.3.5.3.1. *The HAE process* [92, 93], developed at Frankford Arsenal, is an electrochemical process for producing inorganic coatings having excellent corrosion resistance and paint

base qualities on all magnesium alloys. The processing bath contains potassium hydroxide, potassium fluoride, trisodium phosphate, aluminum hydroxide, and potassium manganate in aqueous solution. The bath can be maintained indefinitely by replenishing chemicals. The solution is strongly oxidizing and must not be allowed to come in contact with organic materials. The processing tank is made of black iron or unlined steel, with provision for circulating and cooling the electrolyte. For the bifluoride-dichromate post-treatment often specified, a tank lined with polyethylene, a vinyl, or other inert material is required.

The magnesium alloy should be suitably cleaned (see subsec. 6.3.5.1) before chemical pretreatment. Heavy oxide films or corrosion products should be removed by a chromic acid pickle (other acid pickles should be avoided). Otherwise, a hot alkaline cleaning and cold water rinse is usually adequate. Light chromate films left on the magnesium surface do not interfere with formation of the heavy (Type II) HAE coating; however, such films should be removed from surfaces that are to receive the light (Type I) HAE coating. The process utilizes closely controlled alternating current. Electrical connections to the work and to bus bars must be firmly made with magnesium connectors and leads; the portion of the leads at the liquid-air interface should be protected with vinyl-type electroplater's tape. Parts to be processed are divided into two groups of approximately equal area, each group constituting one of the electrodes. Coatings of different hardness and thickness, and of characteristic color, can be produced from the same chemical bath by varying the operating conditions (current, time, and/or temperature). The current density must be closely controlled throughout the process by the use of suitable control circuits which increase the voltage as required to maintain a constant current as the electrical resistance increases with the build-up of the anodic coating.

Three classes and various grades of HAE coatings, comprising light and heavy types, are covered by specification MIL–M–45202 [93]. Type I, Class A is a light, smooth, tan coating having a thickness of about 0.0002 inch, produced by treatment for 6 to 8 minutes in a bath at room temperature employing a current density of 18 to 20 amperes per square foot maintained over a voltage range from 0 to 80 volts. The anodic coating is then given a hot sodium chromate (1% solution) post-treatment and dried without rinsing. This type of coating is particularly useful for providing a good paint base and good corrosion protection where tolerance requirements, time or cost limitations, or lack of substrate rigidity preclude use of the full, hard brown coating. Alternatively, if a clear coating is to be applied, the chromate

post-treatment may be omitted and the anodic coating instead rinsed thoroughly in cold then hot water followed immediately by dyeing with special solutions. Type I, Class B is the so-called "low voltage coating" produced by treatment for 15 to 20 minutes in a 140 to 150 °F (60 to 66 °C) bath at 9 volts and a current density of about 40 amperes per square foot. The treatment is applicable only to aluminum-bearing magnesium alloys. The low voltage coating is smooth, olive-drab in color, and builds up to about 0.0004 inch but is somewhat softer and more porous than the Class A coating. It is given a hot sodium dichromate (0.3% solution) post-treatment and dried without rinsing.

Type II, Class A is the heavy, hard, brown coating obtained by a full HAE treatment in which the work is immersed for 60 to 90 minutes at room temperature at a current density of 15 to 20 amperes per square foot maintained over a voltage range from 0 to 85 volts. The coating builds up to about one mil (0.001 inch) in thickness and provides the maximum in corrosion resistance and abrasion resistance as well as an excellent paint base. Corrosion resistance is enhanced by post-treatment in a hot sodium chromate solution (1%) or, to an even greater degree, by post-treatment in an ammonium bifluoride-sodium dichromate bath (10% bifluoride, 2% dichromate, room temperature); the post-treatment is followed by drying without rinsing. An additional degree of corrosion resistance to salt spray is imparted if the post-treatment includes artificial aging for several hours in a humidified enclosure heated to about 185 °F (85 °C).

Among the HAE coatings described above, the heavy coating with bifluoride-dichromate post-treatment (Type II, Class A, Grade 3 of MIL–M–45202) is the one most frequently specified and the treatment considered to be the most economical and effective as a base for organic finishes.

6.3.5.3.2. *Acid Chromate Anodic Process* (Dow No. 17).—This is a proprietary process [94] which is applicable to all magnesium alloys. Several classes of these coatings are covered by specification MIL–M–45202 [93]. The process produces coatings that have excellent paint base and corrosion protection qualities, along with good hardness and abrasion resistance. The process utilizes a hot aqueous electrolytic bath containing ammonium bifluoride, sodium dichromate, and phosphoric acid. Either alternating or direct current may be employed, at voltages up to 110 volts. Treatment time depends on the current density (5 to 50 amp/ft^2) and may vary from a minute to an hour. Three types of coating may be produced, depending on the voltage employed; these are: (1) *40-volt clear coating* used as a

base for transparent lacquers or varnishes to impart a final metallic appearance similar to clear anodizing on aluminum; (2) *60 to 75-volt low voltage thin coating* (light green, about 0.0003 inch in thickness) for a good combination of paint base and corrosion protective qualities; and (3) *75 to 90-volt regular full coating* (dark green and about 2 mils in thickness) for the best combination of abrasion resistance, corrosion protection, and paint base qualities. Before treatment, parts should be cleaned in an alkaline cleaner (see subsection 6.3.5.3.1) and thoroughly rinsed with cold water. After anodizing, the parts are rinsed in cold water, followed by a hot water dip or rinse to facilitate drying. (If the anodized parts are to be left unpainted, they should be sealed by immersion for 15 minutes in an aqueous sodium silicate bath maintained at 200–212 °F (93–100 °C) followed by rinsing in cold water then hot water and drying).

6.3.6. Other Metals

The surface preparation and pretreatment of some of the less frequently painted metals are briefly considered in the following subsections.

6.3.6.1. GENERAL.—Metals that are difficult to paint or pretreat chemically should be thoroughly cleaned and, in many cases, roughened before painting.

6.3.6.1.1. *The cleaning process* should remove all oil, grease, soil, dirt, and other foreign matter from the surface. Solvent cleaning (see sec. 6.3.1.1) is of general applicability, although other cleaning methods (section 6.3.1) may be used where appropriate or necessary. Sandblasting accomplishes both cleaning and roughening; where sandblasting is unfeasible or too severe, the use of emery paper can often provide the degree of roughening needed for adequate paint adhesion.

6.3.6.1.2. *The wash primer type of pretreatment* described in section 6.3.2.5, in addition to its wide and effective use on steel, zinc, and aluminum, is also applicable to other metals, including cadmium, copper and its alloys, stainless steel, nickel, chromium, titanium, lead, and terneplate—but not necessarily under all types of topcoats.

6.3.6.1.3. *Proprietary chromate treatments* are available [91a, 95] that provide excellent corrosion protection and impart good paint receptivity to surfaces of zinc, cadmium, copper, brass, bronze, silver, aluminum, and magnesium (chromate treatments for the latter were covered in sec. 6.3.5.2). These chromate treatments employ acidic solutions containing hexavalent chromium ions (derived from chromic acid, dichromates, chromates, or a combination of these), a mineral acid (usually sulfuric), and sometimes an organic acid also. The chromate coatings are formed non-electrolytically by simple immersion of the parts in the chromating bath at room temperature or slightly higher, for periods ranging from a few seconds to a few minutes depending on the type of treatment. Spraying or brushing techniques may also be used in some instances where immersion is not feasible. The chromate coatings produced by these treatments are very thin (0.00002 inch or less) amorphous films with excellent corrosion-inhibiting properties that enhance paint life while protecting the metal.

A number of systems for the preparation and painting of various metal surfaces are specified in MIL–STD–171 (ORD) [96].

6.3.6.2. ZINC AND CADMIUM.—These surfaces should be thoroughly solvent-cleaned to produce a surface completely free of oil, grease, dirt, processing compounds, and temporary protective compounds. Vapor degreasing is preferred. The clean surface, if not previously chromated at the factory, should then be given one of the five pretreatments indicated in the discussion of galvanized surfaces in section 6.3.3. (Sec. 6.3.3 also deals with the problems involved in the painting of factory-chromated galvanized surfaces.)

6.3.6.3. COPPER, BRASS, AND BRONZE.—The surface should be cleaned free of all oil, grease, dirt, and other foreign matter and then roughened by sanding, light sandblasting, or phosphoric acid etching (sec. 6.3.1.5). Alternatively, the clean surface may be given a wash primer pretreatment as described in section 6.3.2.5, or a chromate treatment such as that described in section 6.3.6.1. (Also see sec. 4.3.3).

6.3.6.4. SILVER may be protected against tarnishing by application of a suitable chromate treatment or a protective lacquer or both. The silver should first be cleaned free of oil, grease, fingerprints, tarnish, polishing compounds, and other foreign matter. A proprietary treatment which produces a clear chromate coating on silver is available as indicated in section 6.3.6.1. The chromate coating affords a good base for a clear lacquer if desired.

6.3.6.5. TIN should be solvent-cleaned to remove all oil, grease, dirt, and other foreign matter from the surface. For hot dip tin no further pretreatment is necessary. Electrodeposited tin (deposited from an alkaline stannate bath) should be treated with a hot chromic acid-phosphoric acid aqueous solution (contain-

ing equal weights of each acid and maintained at a pH of 2.0 to 3.0 at 160 to 180 °F [71 to 82 °C]) before application of a protective coating. Baked lacquers make effective coatings.

6.3.6.6. TERNEPLATE should be cleaned (usually by solvent cleaning) free of oil, grease, dirt, and other foreign matter. If feasible, an oxalate or chromate base pretreatment coating should be applied. Otherwise, a wash primer pretreatment coating (see sec. 6.3.2.5) may be applied to the clean surface. Alternatively, a clear varnish size coat is sometimes applied to the clean surface before application of a finish coat. Adhesion is improved if the surface is roughened before application of organic coatings. A conventional iron oxide "roof and barn paint," such as that described by Federal Specification TT–P–31, provides an economical and reasonably durable coating for "roofing tin" (as terneplate roofing is commonly called).

6.3.6.7. LEAD, while needing little protection, is frequently painted to obtain a more pleasing appearance. The surface should be cleaned and roughened before receiving paint. A wash primer pretreatment (sec. 6.3.2.5) may be used to obtain increased adhesion.

6.3.6.8. TITANIUM and titanium alloys that are to receive organic coatings should be solvent cleaned to remove oil, grease, and other foreign matter and then sandblasted. If sandblasting is not feasible, the surface should be given a wash primer pretreatment (as described in sec. 6.3.2.5).

6.3.6.9. STAINLESS STEEL, NICKEL, AND CHROMIUM, because of their noncorrosive nature and intrinsically pleasing appearance, are seldom painted. When an organic coating is desired, the surface should be thoroughly cleaned (preferably by solvent-cleaning) to remove all oil, grease, dirt, and other foreign matter and perhaps roughened slightly with emery paper to promote adhesion. The wash primer type of pretreatment (sec. 6.3.2.5) may also be used on these metals to obtain improved adhesion.

6.4. Preparation of Concrete and Masonry Surfaces

As with other surfaces, a basic requirement in the preparation of concrete and masonry for painting is that the surface be clean: free of dust, dirt, oil, grease, efflorescence, chalk, and loose material. Additional problems in the painting of concrete and masonry surfaces, particularly when new or insufficiently aged, arise from: (1) unbound moisture within the concrete (and in the mortar joints of other masonry) remaining from the original mixing with water, (2) the presence within the material of soluble alkaline substances that are brought to the surface by the outward movement of moisture and deposited as efflorescence, (3) possible contamination with form oil or concrete curing compounds, (4) glazed areas resulting from casting against a smooth, non-absorbent form.

Depending on the condition of the surface and the nature of the coating system to be applied, the proper preparation of concrete and masonry surfaces for painting may involve one or more of the following steps: (1) aging or weathering, (2) cleaning, (3) patching, grouting, and filling, (4) roughening, (5) pretreatment, (6) surface conditioning. These factors are discussed in the following subsections, and the extent to which they must be considered in applying various types of coating systems is indicated.

6.4.1. Aging and Weathering

Where time permits, aging is probably the most convenient and effective single method of preparing concrete and other masonry surfaces for painting. In some cases, as with glazed asbestos-cement shingle, weathering for several years is virtually the only practical way to obtain a surface suitable for painting. Aging permits the concrete to dry out, neutralizes the surface alkalinity, and reduces the inner, free alkalinity through continuing cure and by moisture-borne migration of alkaline substances to the surface where they are gradually neutralized by reaction with the carbon dioxide in the atmosphere.

With the escape of moisture and the reduction in the amount of soluble alkaline substances within the material, efflorescence decreases and eventually ceases for practical purposes. However, efflorescence may recur even after extensive aging if the concrete should again become wet internally.

During weathering, oily contaminants are gradually washed and worn away, and the surface acquires a weathered roughness that provides a good mechanical bond for paint.

While all this is well and good, many months or even years may be required for the practical completion of this aging process, depending on the thickness and porosity of the material and the nature of the service environment. It is frequently impractical to delay painting for such long periods of time. Fortunately, although long aging is necessary for the safe application of oil-base paints, there is now available a variety of water- and alkali-resistant types of coatings which require relatively little aging of the substrate.

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6.4.1.1. LATEX (WATER EMULSION) PAINTS (see sec. 2.3.5), because of their relative insensitivity to water and alkalinity, may be applied on damp, only briefly aged (but not fresh, uncured) masonry surfaces. As a general rule, at least 4 weeks aging is desirable whenever possible. Although the surface may be damp, it should not be wet when the latex paint is applied.

6.4.1.2. CEMENT-WATER PAINTS (see sec. 2.3.9.1) are completely resistant to the moisture and alkalinity in concrete and may be applied virtually as soon as the concrete has set. Little or no aging is required.

6.4.1.3. ALKALI-RESISTANT SYNTHETIC RESIN COATINGS (e.g., epoxies, polyesters, polyurethanes, and various synthetic rubbers) may be applied without long aging of the surface in most instances; however, it is usually essential that the surface be dry. The instructions of the manufacturer usually provide the best guide to the use of such materials.

6.4.1.4. OIL-BASE AND OLEORESINOUS PAINTS may be safely applied only on dry, thoroughly aged concrete or masonry. Where such paints must be applied to concrete that has aged less than a year, it has been suggested [97] that a *pretreatment* consisting of an aqueous solution containing 2 percent zinc chloride and 3 percent phosphoric acid be applied to the surface and allowed to dry upon it without rinsing. After drying, loose salts should be removed by light dusting, but the adherent encrustation of insoluble salts should be left on the surface. The application of dilute zinc sulfate solution to concrete to reduce the surface alkalinity, although a popular practice in the past, is no longer considered to be an effective treatment because it may leave soluble salts on the surface that may increase the tendency toward blistering of the paint film.

6.4.2. Cleaning

The cleaning methods used should remove dirt, dust, oil, grease, efflorescence, loose chalk, and other loose material or foreign matter from the surface (see applicable parts of sec. 6.3.1). Latex paints have good resistance to moisture and alkalinity, but because of their nonpenetrating nature and poorer wetting properties they require more thorough surface preparation than solution-type coatings, particularly with respect to removal of all loose chalk. Even a moderately chalky condition is not a satisfactory base for latex paint; a suitable surface conditioner (see sec. 6.4.6) that will wet and penetrate the chalk must be used to obtain satisfactory adhesion of the latex

paint. A moderate degree of chalking is not a problem with oil-base paints, since these effectively penetrate and bind the chalk.

6.4.2.1. DUST, DIRT, AND LOOSE MATERIAL frequently can be removed from the surface merely by bristle-brushing or by hosing down with clean water. When necessary, scraping, wire-brushing, or sandblasting may be employed to dislodge foreign matter; such mechanical methods should be followed by hosing down with water.

6.4.2.2. FORM OIL, grease, and other oily contaminants are eventually removed by weathering, although many months may be required, depending on the degree of contamination and the severity of the weather. In the absence of adequate weathering, oily contaminants should be removed either by (1) scrubbing with a solution of trisodium phosphate (4 oz. per gallon of water) followed by thorough rinsing of the surface with clean water, or (2) etching the surface with a 5–10 percent solution of muriatic (hydrochloric) acid in the manner described below for the removal of efflorescence. When the latter (acid) treatment is used, it must be followed either by thorough rinsing with clean water or by neutralization with trisodium phosphate solution or ammonia water (10%) followed by thorough rinsing with plain water.

The choice as to whether an acid or an alkaline cleaning method should be used, and whether—in the case of acid cleaning—to use only a clean water rinse or to neutralize before rinsing, depends on the nature of the coating system to be applied. Since many latex emulsions are alkaline in nature and therefore acid-sensitive (such is the case with styrene-butadiene latexes and with acrylic latexes), alkaline cleaning or neutralization of acid with trisodium phosphate solution is usually recommended as a precaution against breaking of the emulsion when it is applied to the surface. On the other hand, this may not be a critical factor with polyvinyl acetate latexes which are normally slightly acidic. With oil-base or oleoresinous coatings, which are alkali-sensitive, alkaline washes are best avoided. Where specialized synthetic resin coatings are to be used, the instructions of the manufacturer should be followed.

Oily contaminants can be removed from the surface by mechanical methods if desired. Traces of oil can be removed by rubbing the surface with steel brushes or coarse abrasive stones. However, if the surface is generally contaminated, it is much more effective to lightly sandblast the area to be painted, or else to postpone painting until the oil has been removed by the action of the weather. Mechanical cleaning methods should be followed

by hosing down the surface with water to wash away all loose debris.

6.4.2.3. EFFLORESCENCE, when present, must be completely removed before painting is attempted; otherwise, it will spoil both the appearance of the paint job and its performance. It has already been indicated that efflorescence is caused by the moisture-borne migration of soluble alkaline salts from the interior of the material to the surface where the salts are deposited as a whitish bloom or encrustation. The removal of efflorescence is best accomplished by sandblasting, if possible; otherwise, abrasive stones or wire brushing may be employed, followed by treatment with dilute muriatic (hydrochloric) acid. An acid concentration of 5 to 10 percent is usually employed, but concentrations as high as 20 percent are sometimes used. The surface is first wet with water, then the acid is applied liberally and allowed to remain on the surface for about five minutes. The surface is then scrubbed with a stiff brush and thoroughly rinsed with clean water to remove all traces of acid. If necessary, the treatment is repeated, until all efflorescence has been removed. A neutralizing rinse with trisodium phosphate solution or ammonia water is often recommended when certain types of latex paint are to be applied, as indicated in the preceding subsection. The neutralizing solution, in turn, should be thoroughly rinsed away with clean water.

6.4.2.4. MILDEW or MOLD if present (usually only on previously painted or organically contaminated surfaces) should be removed by scrubbing with trisodium phosphate solution (4 oz. per gallon of water) or with a 5 percent solution of sodium hypochlorite such as the common household chlorine bleach, followed in either case by thorough rinsing with clean water.

6.4.3. Patching, Grouting, and Filling

Large cracks, holes, and other damaged areas should be repaired by *patching* with a suitable material such as the commercially available cement-sand mixtures, latex-concrete mixtures, stucco patch, or other cementitious materials that are formulated for this purpose. Adequate time for drying or aging of repairs should be allowed before painting. Open-textured masonry surfaces such as cinder block should be given a grout coat or a fill coat, depending on the type of coating that is to be applied. A *grout coat* consisting of a 50:50 cement-sand mixture provides an excellent base for cement water paints. The grout coat, like cement water paint, must be kept damp while curing for the first 48 hours to ensure proper hydration of the cement and freedom from cracking or

powdering. When a latex paint is to be used, it is preferable to employ a special *fill coat* made by combining white portland cement, washed silica sand, and water with a mixing liquid containing the same latex polymer that is used in the latex paint to be applied. In some cases, some of the latex paint itself is added to the fill coat mixture. Formulas for fill coats are given in the applicable Federal Specifications for latex paints [5, 6, 7]. Such fill coats do not require damp curing; however, they should be allowed to dry for 24 hours before painting. Since both fill coats and grout coats such as those described above are alkaline in nature, it is unsafe to use them under oil-base or oleoresinous paints unless adequate time for aging (at least 90 days) can be allowed (see preceding sec. 6.4.1).

6.4.4. Roughening

Some concrete surfaces are so dense, or glazed from having been cast against a smooth or nonabsorbent form, that good paint adhesion is difficult to obtain. Such surfaces should be roughened before painting. This is best accomplished by light sandblasting where feasible. Alternatively, the surface may be etched with a 5 to 10 percent solution of muriatic (hydrochloric) acid. The surface should be wet down with water before applying the acid. The acid etching process should be continued until the surface acquires the texture of a fine sandpaper. The surface should then be rinsed thoroughly with clean water. Where specified for the particular type of paint to be used, the surface may be given a neutralizing alkaline rinse with dilute trisodium phosphate solution or ammonia water, as discussed in the preceding subsection 6.4.2.2 on cleaning, before rinsing thoroughly with clean water.

When neither light sandblasting nor acid etching are feasible, the glazed or dense surface may be roughened by rubbing it with coarse abrasive stones.

6.4.5. Pretreatment

Chemical pretreatment of concrete and masonry surfaces, other than treatment with hydrochloric acid as already mentioned for etching the surface or for the removal of efflorescence, is largely limited to situations in which oil-base or oleoresinous paints are to be applied to surfaces which have not been adequately aged. In such cases, the pretreatment with zinc chloride-phosphoric acid solution described above under Aging (sec. 6.4.1) is thought to be beneficial on the basis of available evidence [97]. This pretreatment, however, has not had wide use because only a limited amount of oil-base or oleoresinous paint is used on masonry surfaces today, now that

the water- and alkali-resistant latex paints are available. At best, pretreatment must be considered as less effective than thorough aging in producing a paintable surface.

6.4.6. Conditioning of Chalky Surfaces

The nonpenetrating character of latex paints which gives them their excellent sealing properties on porous surfaces of concrete and masonry is associated with low wetting properties that prevent the development of good adhesion to chalky surfaces. Previously painted concrete or masonry surfaces that exhibit chalking not practicable to remove by sandblasting should be brushed as free as possible of loose chalk and then treated with an alkali-resistant, penetrating type of surface conditioner before application of latex paint. A typical surface conditioner suitable for this purpose may be a relatively low viscosity coating based on a tung-oil phenolic resin or a soya- or linseed-oil alkyd of long oil-length in an organic solvent thinner, possibly together with a small proportion of pigments and extenders (also see sec. 2.4.3). A number of proprietary products for this purpose are available and are usually included as part of the manufacturer's line of latex coating systems. The surface conditioner penetrates and binds the chalk and provides an adherent base for the latex paint. Even the use of a surface conditioner is not adequate when the masonry surface is in poor condition with heavy chalking

or multiple layers of weak cement-type paints; in such cases, sandblasting is the only effective method of preparing the surface (also see sec. 6.6.4.1).

6.4.7. Summary

The nature and degree of surface preparation required for concrete and masonry before painting depends to a large extent on the nature of the coating system that is to be applied. In all cases the surface should be sound, free of dirt, oil, efflorescence, and loose material, and rough enough to provide for good mechanical bonding of the coating. Where practicable, light sandblasting provides the best surface preparation; it is not, of course, a substitute for aging where the latter is required. Open-textured masonry surfaces should receive a grout or fill coat before painting. Cement-water paints may be applied on damp, unaged concrete and masonry and on surfaces previously painted with cement-water paint, even if chalking or dusting is present, so long as the old coating is firmly adherent. Latex paints may be applied on damp, relatively briefly aged surfaces that are clean and free of chalk; when all loose chalk cannot be removed, a penetrating liquid surface conditioner should precede application of the latex paint. Oil-base and oleoresinous paints may be safely applied only on dry, well-aged concrete and masonry surfaces that are not likely to become internally wet again during service after painting.

6.5. Preparation of Plaster and Wallboard Surfaces

Plaster and wallboard surfaces require relatively little preparation for painting; however, as in any painting, it is essential that the surface be sound and clean. Since plaster and wallboard are porous materials, the clean surface must be properly sealed to obtain good hold-out and uniform appearance of topcoats. Latex primer-sealers are particularly suitable for this purpose because of their nonpenetrating nature, but their lower wetting ability necessitates a cleaner surface than is required for solution-type coatings. Both latex-type and oleoresinous primer-sealers are discussed in sections 2.4.4 and 4.5. Application of the proper primer-sealer allows the use of virtually any type of topcoat.

6.5.1. Plaster

To achieve a good finished appearance, it is necessary that cracks, holes, indentations, and other defects be repaired before painting. This can be accomplished by filling the damaged areas with spackling compound or patching plaster. To obtain a good anchor for the patch

where large cracks or holes are involved, it is desirable to undercut the edges of the area to be filled and to wet the edges with water to prevent excessive loss of water from the patching material into the adjacent plaster. (Very large holes or areas of loose plaster should, of course, be replastered before painting.) After the repaired areas have dried for at least three days, they should be sanded smooth with fine sandpaper.

6.5.1.1. NEW PLASTER, because of its high moisture content and alkalinity, should be allowed to age for 60 to 90 days before application of oleoresinous paints. Where latex paints are to be applied, at least two weeks of aging is highly desirable, and a month or more should be allowed whenever practicable. Apart from aging, new plaster frequently needs only to be dusted to prepare it for painting.

6.5.1.2. OLD PLASTER or plaster that has become soiled should be washed with clean water. If a latex primer-sealer is to be applied, it is permissible to use a mild detergent such as

trisodium phosphate solution as a cleaning aid, followed by a clean water rinse. Excessive wetting or soaking of the plaster should be avoided.

Oily contaminants, if present, must be removed to obtain good paint adhesion. Although this can be accomplished by washing the surface with a detergent solution, it is usually preferable, especially where an oleoresinous coating system is to be applied, to "dry clean" the surface by wiping or washing it with a suitable solvent such as mineral spirits. Wet surfaces must be allowed to dry thoroughly before application of oleoresinous paints. Latex paints may be applied while the surface is still damp, but not wet. Painting with latex coatings may, therefore, advantageously begin soon after washing of the surface is completed, thus minimizing the possibility of recontamination.

6.5.2. Wallboard

A number of different kinds of wallboard (including prefinished wallboard) are available under a somewhat confusing variety of generic and proprietary names. For practical painting purposes, these may be considered within two broad categories: (1) Those which are essentially paper-covered inorganic plasters, frequently alkaline in nature, or which are joined or finished with alkaline plasters, as typified by the common gypsum wall board or "dry wall" construction (also known as "sheet rock"

or plasterboard), and (2) non-alkaline, organic composition boards composed of compressed and/or resin-bound wood or cellulose fibers in a variety of physical forms, and known by such designations as beaverboard, fiberboard, hardboard, Masonite, pressed wood, etc.

6.5.2.1. GYPSUM WALLBOARD consists of a core of gypsum plaster sandwiched between exterior skins of heavy, felted paper. In dry wall construction, the sheets of wallboard are butted together and nailed to the studs. The nails should be countersunk and covered with joint cement. All joints should be filled with joint cement, taped, and plastered. When dry, the assembly should be sanded smooth leaving feathered edges. Care in sanding is required to avoid roughing up the paper surface. After sanding, the surface should be wiped free of dust, preferably with a damp sponge; it is then ready to receive an emulsion-type primer-sealer. Solution-type oleoresinous primer-sealers are not satisfactory for use on gypsum wallboard because they tend to raise the nap of the outer paper layer.

6.5.2.2. FIBERBOARD, HARDBOARD, and other nonalkaline wallboards based on wood or cellulose fibers should have all nails countersunk, the holes filled with spackling compound, and sanded smooth. The surface should be brushed or vacuumed to remove all dust and is then ready to receive either a latex primer-sealer or an oleoresinous solution-type primer-sealer.

6.6. Preparation of Previously Painted Surfaces

The amount of surface preparation required for a previously painted surface depends on the condition of the old paint, the nature and condition of the substrate, and the kind of paint to be applied in repainting. Surface preparation is an integral part of the general problem of maintenance painting discussed below.

6.6.1. Maintenance Painting

All organic coatings eventually deteriorate or wear away and therefore require periodic renewal. Since the service life of the coating will vary widely with the type of coating and the nature of the service environment, no fixed interval between repainting can be stated. However, when accurate records of paint jobs are kept, the history can provide a good estimate of when repainting may be needed, for purposes of advance planning. The actual time to repaint should be determined by periodic examination of the surface, since the cost of repainting is closely tied to the condition of the coating and substrate.

The essential elements of an effective and economical maintenance painting program are:

(1) *Periodic careful inspection* of the painted surface, with touch-up painting where needed for damaged or exceptionally worn areas; (2) *repainting at the right time*, when the old paint is well-worn but not so badly deteriorated as to require extensive or complete removal, and before the substrate itself is exposed to deteriorative influences; (3) *adequate surface prepartion* which will remove all loose paint and foreign matter, leaving a clean, sound surface for the new paint; and (4) *selection of a suitable recoating system* that will bond properly to the old paint, or to the substrate where it is exposed. Provided that the old paint system gave satisfactory service the choice of a similar system will assure compatibility.

Repainting at the right time minimizes the labor and expense of surface preparation. Paint worn thin but still firmly bonded to the substrate need only be dusted or washed to ensure a clean surface before repainting. On the other hand, in situations where the old paint has been permitted to deteriorate to the point of extensive cracking, curling, or peeling—or where the substrate has been laid bare and damaged or corroded—it may be necessary to

expend a great deal of effort and time in completely removing the old paint and in cleaning dirt or corrosion products from the substrate. In the latter case, the cost of surface preparation may be considerably greater than the cost of paint and painting.

Painting too often or too soon also should be avoided. Not only is this uneconomical but it ultimately results in the build-up of an excessively thick coating that may be brittle and prone to cracking and chipping, particularly on dimensionally unstable substrates such as wood or thin metal.

Mildew or mold may form on coatings in warm, damp climates or locations. Before repainting is done, the fungus should be removed by scrubbing the surface with a solution of trisodium phosphate (4 oz. per gallon of water) or with a 5 percent sodium hypochlorite solution such as the common household chlorine bleach, followed in either case by thorough rinsing with clean water. It is desirable to remove mildew or mold whenever it is noticed during the periodic maintenance inspections, since if allowed to remain it will cause progressive destruction of the coating.

The criteria which determine the right time for repainting, and the problems encountered and procedures to be followed in maintenance painting, are somewhat different for different types of substrates in various environments. Surface preparation for the maintenance painting of the various types of substrate is discussed in the following sections.

6.6.2. Previously Painted Wood Surfaces

The preparation of previously painted wood surfaces for repainting has been fully discussed in section 6.2.2.

6.6.3. Previously Painted Metal Surfaces

Preventive maintenance in the form of periodic touch-up painting of localized areas that show excessive wear, damage, or rusting is an important factor in obtaining maximum service life from coatings on metal surfaces. The localized bad spots can be cleaned by wire brushing, then spot-primed and repainted with very little difficulty or expense.

At the stage in the life of the coating when it is well-worn but still performing its protective function in all but a few localized areas, the protection can be prolonged and the labor and expense of extensive surface preparation can be avoided by application of a single overall coat of paint. In such cases, localized bad spots should be wire-brushed and spot-primed, and the entire surface should be cleaned free of dust, dirt, oil, grease, and foreign matter by washing with a mild detergent solution or—where considerable oil or grease is present—

by washing with solvents as described in section 6.3.1.1. The clean and spot-primed surface is then ready to receive a full coat of paint, preferably of the same type as before to assure compatibility with the old paint.

When the coating failure is general, as evidenced by numerous and widely distributed rust spots, or by widespread peeling, flaking, blistering, or exposure of bare substrate, it is necessary to remove the old paint completely and to clean the metal surface properly before repainting can be done successfully. Removal of the old paint and cleaning of the surface can be accomplished simultaneously by the methods of sandblasting, flame cleaning, or alkali cleaning described in section 6.3.1 (subsecs. 6.3.1.8, 6.3.1.9, and 6.3.1.4, respectively). Alkali cleaning does not remove rust. Of the several methods of paint removal and surface preparation mentioned, sandblasting is by far the most effective where feasible.

6.6.4. Previously Painted Concrete and Masonry Surfaces

6.6.4.1. LATEX (EMULSION) PAINT.—If the old paint is well-worn but in basically good condition—that is, free of excessive chalking, flaking, blistering, or peeling—the necessary surface preparation before repainting with latex paint may involve only a thorough washing with clean water, or with a detergent such as trisodium phosphate solution followed by a thorough clean water rinse, to remove dust, dirt, oily contaminants, and loose material from the surface.

Loose or heavily chalked surfaces, particularly of cement-type paints, cannot be satisfactorily repainted. Not only is paint adhesion to such surfaces poor but failure will occur within the chalk layer itself through crumbling and distintegration. Lightly chalked surfaces may sometimes be satisfactorily prepared by removing as much chalk as possible by brushing and washing followed by treatment of the surface with a penetrating type surface conditioner as described in section 6.4.6. However, the only completely effective way to prepare a heavily chalked surface or a surface with multiple layers of weak cement paint for satisfactory repainting is to remove the chalk or cement paint thoroughly by sandblasting. Where sandblasting is not feasible, power wire brushing methods may be employed, but with greater labor and less satisfactory results.

Complete removal of the old paint in the area of failure is also indicated when the paint is blistering, flaking, or peeling. Such failure, particularly if accompanied by efflorescence or discoloration, is usually caused by excessive moisture coming from within the concrete or masonry surface. Where the source of the

moisture is from outside the masonry (e.g., from the ground on the exterior of a wall below grade) then the source will have to be eliminated through better drainage or by exterior waterproofing before successful repainting can be accomplished.

6.6.4.2. SOLVENT-THINNED PAINTS of the oil-base or oleoresinous type, while less moisture- and alkali-resistant than latex paints, have better wetting and penetrating properties and therefore require less stringent surface preparation. Moderately chalked areas of firmly attached paint (including old but sound cement-water paint) ordinarily require only brushing to remove loose chalk and soil from the surface. If oily contaminants are present, they can be removed by washing with mineral spirits or other suitable solvent. The surface must be thoroughly dry when repainting. Blistering and peeling or other evidence of moisture failure preclude the application of oil-base or oleoresinous paints unless the source of the moisture can be completely eliminated. Loose paint in localized areas should be removed by brushing or scraping. Where the paint is in generally poor condition, with widespread flaking or peeling, complete removal by sandblasting or power wire-brushing is indicated.

When repainting is to be done with solvent-thinned or 100-percent-solids coatings based on specialized synthetic resins, the instructions of the manufacturer concerning surface preparation should be closely followed.

6.6.4.3. CEMENT-WATER PAINTS (see sec. 2.3.9.1) may be applied directly over firmly adherent cement-type paints, even if chalking or dusting is present; brushing with a stiff brush is usually the only surface preparation required. However, if the old cement paint is crumbling, flaking, or scaling, it should be completely removed by sandblasting, or by treatment with hydrochloric acid in the manner described for the removal of efflorescence (sec. 6.4.2). Old coatings of whitewash (see sec. 2.3.9.2) also should be completely removed with

hydrochloric acid before repainting. Cement-water paints will not ordinarily adhere to organic coatings; the latter must be completely removed, preferably by sandblasting, before repainting.

6.6.5. Previously Painted Plaster and Wallboard Surfaces

The surface to be repainted should be clean and sound. Damaged areas should be repaired by filling with spackling compound or patching plaster and sanding smooth. All loose or blistered paint should be removed by scraping and the surrounding area sanded to a feather edge. Dust, dirt, and moderate amounts of oily contaminants may be removed by washing with a detergent such as trisodium phosphate solution (4 oz. per gallon of water). Where considerable oily contamination is present, it is preferable to solvent-clean the surface (see sec. 6.3.1.1) with a grease solvent such as mineral spirits. "Dry cleaning" with solvent is especially desirable if oleoresinous paint is to be applied, since it eliminates the need to allow time for thorough drying. If all chalk cannot be removed, an oleoresinous paint may provide better adhesion than the latex type. The latter, however, may be applied while the surface is still damp (but not wet) from washing.

If blistering and efflorescence are in evidence, the presence of excessive moisture in the wall is indicated, and the source of the moisture should be located and eliminated, if possible, before repainting.

If the paint is in poor condition as evidenced by general scaling, cracking, blistering, peeling, etc., then the old paint should be entirely removed with a solvent-type paint remover such as that covered by Fed. Spec. TT–R–251 or Mil. Spec. MIL–R–46073. Such paint removers contain toxic volatile solvents which may also be flammable, and they must be used with caution and adequate ventilation. If the paint remover contains wax, as is usually the case, the stripped surface must be washed off with mineral spirits before proceeding with sealing and painting.

6.7. Summary

The foregoing chapter has emphasized the fundamental importance of proper surface preparation in obtaining maximum service life from the applied coating and has presented detailed instructions for the cleaning and pretreatment (if necessary) of virtually all types of surfaces likely to be painted. Cleaning methods have been described in detail primarily in the discussion of steel surfaces (sec. 6.3.1) where they find their widest spectrum of applicability; thereafter, to conserve space, these cleaning methods have been referred to as needed to indicate their applicability to other types of surfaces. The pretreatment of metal surfaces has been comprehensively covered and includes not only steel but also surfaces of aluminum, magnesium, zinc, copper, and other metals.

While the bulk of the presentation has dealt with the preparation of new or previously unpainted surfaces, the preparation of previously painted surfaces has also been considered, in relation to the general problem of maintenance painting. When the old paint is completely removed, the principles of cleaning and pretreating the bare surface are similar to those for previously unpainted surfaces.

As a general rule to be adhered to whenever possible, surface preparation should be followed as soon as practicable by application of the priming paint, before the clean surface can again become soiled or corroded.

The detailed information that has here been presented, in conjunction with the general information given in chapter 4 on the basic types of surface preparation required or considered adequate for particular types of substrates and environments, should provide a practical basis for preparing virtually all surfaces for painting.

FIGURE 6.1. *Glossmeter measures specular reflectance of surfaces and coatings as described in ASTM Method D 523-66T.*
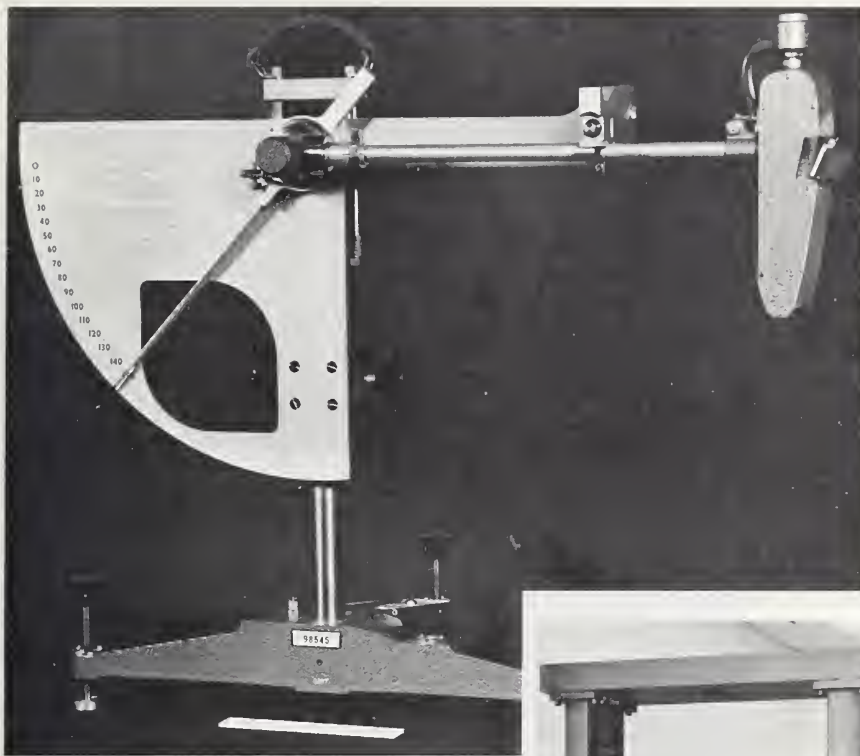
FIGURE 6.2. *Portable impact-type slipperiness tester for measurement of relative slipperiness of different walkway surfaces for various types of footwear, as described in ASTM Method E 303-66T.*
A mechanical heel of leather or rubber forms the lower part of the pendulum and sweeps over the surface when the pendulum is released. Height of swing beyond surface indicates "antislip coefficient."

FIGURE 6.3. *Versatile testing machine provides both light and heavy-duty measurement of stress-strain properties over a wide range of loading and elongation rates, as described in ASTM Method D 2370-65T.*

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FIGURE 6.4. *Spreading a latex grout coat onto a spalled concrete surface.* (Photo courtesy of Paint and Varnish Production.)

FIGURE 6.5. *Trowel finishing latex mortar as a new topping over grout-coated old concrete surface.* (Photo courtesy of Paint and Varnish Production.)

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7. Consolidation of Coatings Information

7.1. A Glance Backward and Forward

Previous chapters of this publication have dealt with major areas of the organic coatings field, including: A description of the types of coatings that are available (chapter 2); a detailed discussion of the properties of synthetic resins on which most modern coatings are based (chapter 3); presentation of a basis for the selection of coating systems for specific purposes (chapter 4); instructions for the storage, safe handling, and efficient application of organic coating materials (chapter 5); and detailed information on the preparation and pretreatment of surfaces that are to receive organic coatings (chapter 6).

Subsequent chapters present a tabular summary of Federal Specifications for organic coating materials (chapter 8), and a selected bibliography of works in the coatings field (chapter 9). Finally, a comprehensive Index is provided. The aforementioned tabular sum-

mary is preceded by a quick guide list that provides a key to the information in the tables; together, they constitute a comprehensive source of information relating to Federal Specifications for organic coating materials.

Considerable information relating to the nature and arrangement of the subject matter presented in this publication, and guidance in its effective utilization, is given in the Preface and in Chapter 1. A careful reading of these sections will prove very worthwhile. In section 1.3 is given a description, with examples, of the manner in which the Index has been organized to provide maximum coverage and utility with a minimum number of entries.

The present chapter rounds out the material presented by providing important supplementary information and by furnishing examples of use of the monograph in solving typical coating problems.

7.2. Supplementary Information

The following sections present general information, important details, and helpful hints not covered elsewhere in the text.

7.2.1. Painting Conditions

The ideal time for painting is during warm, dry weather. In any case, the painting should be done under favorable atmospheric conditions that will promote proper drying and avoid condensation of moisture on the uncured film. As a rule, exterior painting should be done only in clear, dry weather at moderate temperatures (45 to 95 °F [7 to 35 °C] are the nominal limits usually specified). When the surface and the paint are cold, there is a greater possibility of condensation, drying is slower, the tendency to run or sag is greater, and the extra thinner required to reduce the paint viscosity for proper application may unbalance the formulation with adverse effects on spreading rate and film properties (see sec. 5.3.2 for a discussion of the principles of proper thinning). Under high humidity conditions, even in warm weather, again drying is slowed, condensation is very likely to occur, and the addition of blush-retardant thinner may adversely effect the film properties. Outside painting should never be done in rain or snow, or when dew or frost is present on the surface. On days when a sharp drop in temperature of 20 degrees Fahrenheit or more is expected, it is inadvisable to do any painting later than mid-afternoon. Such a temperature drop will frequently chill the air

below the dew point and result in the deposition of dew or frost upon the uncured paint film.

While latex paints are not sensitive to moisture in the same sense that organic solvent-type paints are, they will not dry well under humid conditions and will not withstand rainfall occurring during or shortly after their application. Although they may be applied without difficulty on damp or lightly wet surfaces, they should not be applied to materials that are water-soaked or to surfaces covered with heavy dew or with frost. (Cement-water paints preferably are applied to surfaces that have been thoroughly dampened with water, but they cannot be used in freezing weather.) Latex paints may suffer from poor coalescence at temperatures below 50 °F (10°C), and their use at near-freezing temperatures is completely precluded.

The upper temperature limit for satisfactory painting, while nominally given as 95 °F (35°C), is actually determined by the nature of the coating material. Neither the atmospheric temperature nor the temperature of the surface to be painted should be so high as to cause blistering or pinholing of the paint film through too-rapid evaporation of solvent, or poor leveling and faulty surface appearance because of abnormally fast setting of the film. In practice, this seldom happens except with fast-drying lacquers or when paints are applied to surfaces exposed to the hot sun; such surfaces, particularly if metal, may be considerably hotter than the ambient atmosphere. It is for this

reason that painting in the hot summer sun is not considered to be good practice.

Interior painting can often be done when weather conditions preclude outdoor painting; however, it is generally desirable to do interior painting during warm, clear weather when windows and doors can be left open to provide the ventilation needed to prevent dangerous build-up of toxic or flammable vapors. In the latter respect, latex paints with their freedom from fire and toxicity hazards are more suitable for year-round painting.

In general, painting should begin as soon as possible after surface preparation (including adequate time for drying) has been completed —before the clean surface can again become soiled or corroded. In multiple-coat systems, it is desirable that subsequent coats be applied without prolonged delays which might contaminate the surface or adversely affect intercoat adhesion.

7.2.2. General Coating Requirements

7.2.2.1. THICKNESS.—The number of coats of paint required for a particular application is determined by the film thickness needed to accomplish the desired protective or decorative function and by the film build per coat. The latter in turn depends on the spreading rate and solids content of the applied coating.

7.2.2.1.1. *Spreading rate* is the area covered by a unit volume of coating material, usually expressed in terms of square feet per gallon. Spreading rate is directly related to wet film thickness by the equation

$$T_w = \frac{231.0}{144.0 \times S}$$

where T_w is the wet film thickness in inches, and S is the spreading rate in square feet per gallon. Tables and graphs giving the computed relationship are readily available in various paint manuals and handbooks [40, 98]. For convenience, a few representative values are given in the table below:

Wet film thickness (mils)	Calculated spreading rate (ft²/gal)	Spreading rate (ft²/gal)	Calculated wet film thickness (mils)
1.0	1604	1600	1.00
1.5	1069	1300	1.23
2.0	802	1000	1.60
2.5	642	700	2.29
3.0	535	650	2.47
3.5	458	600	2.67
4.0	401	550	2.92
4.5	356	500	3.21
5.0	321	450	3.56
6.0	267	400	4.01
7.0	229	350	4.58
8.0	201	300	5.35
9.0	178	250	6.42
10.0	160	200	8.02
		150	10.69

The dry film thickness can be calculated by multiplying the wet film thickness by the volume fraction of nonvolatile vehicle plus pigment in the whole paint.

In general, the thicker the coating is, the greater are the durability and protection provided, up to the point where the coating becomes so thick and inflexible that it is prone to crack and chip away from the substrate. Also, several thin coats provide better insurance against pinholes and holidays than a single thick coat because of the improbability that such flaws would occur at exactly the same point in successive layers of paint. Coatings that serve chiefly a decorative function in mild service environments need not be as thick as coatings that must withstand rigorous service in corrosive or abrasive environments. For optimum service performance, it is important that the coating be applied at the spreading rate recommended by the manufacturer or in the applicable specification, so that the proper final film thickness will be obtained. Recommended spreading rates normally take into account the nature of the surface and differences in coverage requirements with succeeding coats, as well as the composition and function of the coating material and the nature of the service environment. While spreading rates therefore may vary widely with different materials and applications, the following discussion of typical surfaces and coating materials may serve as a guide while emphasizing the importance of adhering to recommended spreading rates.

For adequate film build on rough, porous surfaces such as concrete and masonry, a considerably lower (heavier) spreading rate is required for the first or primer coat than for subsequent coats, to allow for absorption and for the filling of pores and crevices. For example, the priming paint (perhaps a properly thinned latex paint) might be applied at a spreading rate of only 20 square feet per gallon, while the unthinned finish paint might be spread at the rate of about 600 square feet per gallon.

Wood, also, is a porous material which requires a lower spreading rate for the priming paint than for subsequent coats. For commonly used paints on exterior wood surfaces, the optimum total dry film thickness is 4 to 5 mils (0.004 to 0.005 inch). This is readily achieved with a three-coat system comprising one primer coat and two finish coats. The primer is normally applied at a spreading rate of about 450 square feet per gallon, and each coat of finish paint at about 650 square feet per gallon. Two-coat systems (one coat of primer and one finish coat) capable of building up a 4-mil dry coating thickness also are available. Such systems utilize specially formulated paints having a relatively high solids

content and applied at a low (heavy) spreading rate. In practice, heavy spreading rates without the development of runs, sags, or other faults are difficult to achieve except by skilled painters working under favorable temperature and humidity conditions.

The spreading rates of paints commonly applied on plaster and wallboard surfaces are, in general, similar to the requirements for wood surfaces.

On smooth nonporous surfaces such as metal, optimum spreading rates may be very different for different primers and finish coats, depending on their composition and function and on the over-all thickness requirements of the application. Thus, a zinc chromate primer on aluminum is most effective when applied in a very thin coat (0.4 to 0.6 mil dry film thickness) at a spreading rate of about 1600 square feet per gallon, while a zinc yellow-iron oxide primer on steel may be spread at the rate of about 650 square feet per gallon, and the primer coat in a vinyl resin coating system may be applied at only 250 square feet per gallon. Finish coats in an oleoresinous paint system typically may be applied at a spreading rate of about 550 square feet per gallon, while body and finish coats in a heavy duty vinyl coating system may be applied at only 150 to 200 square feet per gallon. Dry film thickness requirements may range from 3 mils in a two-coat paint system for mild exposure, to 5 mils or more in a typical four-coat oleoresinous paint system for severe atmospheric exposure, and to about 12 mils in the six-coat vinyl resin coating system for steel subjected to severe exposure under continuous immersion in salt water.

With so many variables affecting spreading rate, the value of having and of following a specification or the manufacturer's recommendations is quite apparent.

When repainting, the thickness of new paint applied should, ideally, merely replace the paint that has been worn away, to restore the original coating thickness. As already noted, the build-up of excessive film thickness can result in stresses within the coating and at the coating-substrate interface that may cause premature coating failure by cracking and chipping. Excessive thickness is most likely to cause failure on dimensionally unstable surfaces, such as wood. When doing interior repainting, it should be remembered that indoor coatings do not wear away like coatings exposed to the weather, and repeated repainting may eventually build up a very thick unsatisfactory film. It is a good rule, when repainting little-worn interior surfaces, to limit the thickness of the applied paint to the minimum needed to hide the old surface properly.

In all painting, care should be taken to apply the coating at as uniform a thickness as possible. Spreading rates have little meaning in terms of coating system durability and appearance if the paint is not evenly spread. In critical coating applications or where doubt exists, it is advisable to measure the wet film thickness at intervals during the painting process; also, if feasible, the dry film thickness should be measured in a representative number of locations to provide a final check on the quality of the job.

7.2.2.1.2. *Thickness measurement.*—Some of the instruments that are useful for the measurement of coating thickness are described briefly in the following pages. Detailed discussions of such instruments may be found in the specific references cited and in references [98] and [161].

Wet film thickness can be measured readily and nondestructively on any reasonably smooth, flat, rigid surface by standard methods [99] employing readily available test instruments, such as the Interchemical or Pfund gages. The Interchemical Wet Film Thickness Gage is essentially a triple wheel, having an eccentric recessed inner wheel concentric with and affixed to circular outer rolling wheels; when the gage is rolled over the wet surface, the wet film thickness is indicated by the point at which the paint first contacts the eccentric wheel. The Pfund Gage utilizes a convex lens of calibrated curvature, which is pushed through the wet film to the substrate; from the known radius of curvature and the diameter of the paint spot produced on the convex lens, the wet film thickness can be calculated.

Dry film thickness on non-metallic substrates cannot be measured nondestructively by presently available methods. On sheet or panel material amenable to measurement by dial gage or micrometer [100, 101], the nominal coating thickness can be computed as the difference between the thickness of the coated and the uncoated (or stripped) material. Other devices, such as the Gardner Scratch (Saw-tooth) Thickness Gage, employ calibrated scratching or penetrating wheels or tools as a means of measurement. A simple, pencil-like "go-no go" gage [103] equipped with three fine teeth scaled to scratch the paint surface to specified depths has been proposed for use in the field by the Federal Housing Administration. A recently-introduced Paint Inspection Gage [104] combines a precision V-groove cutting tool with a 50-power gaging microscope that permits observation of film thickness and other visual characteristics of the applied film. While these instruments (dial gage and micrometer excepted) for measuring dry film thickness on nonconductive substrates have not yet been adopted as standard methods, they represent useful approaches to a basically difficult problem.

On metallic or conductive substrates the meas-

urement situation is much better. Measurements of dry film thickness on such surfaces can be made non-destructively, with ease and speed, by standard methods employing readily available instruments that operate on magnetic or electronic principles, in conjunction with reference standards of known coating thickness. On magnetic (ferrous) substrates, an instrument such as the Aminco-Brenner Magne-Gage, operating on the magnetic principle, can be used [102, 105]. In essence, this instrument when calibrated measures the force required to pull a permanent bar magnet from the coated surface. Since the magnetic attractive force is a function of the distance between the bar magnet and the magnetic substrate, it is similarly related to the thickness of the intervening nonmagnetic coating material, as given by a calibration curve obtained from measurements on standard panels of known coating thickness. While the Magne-Gage is capable of a high order of precision, even on very thin coatings, it is basically a laboratory instrument which requires a level, vibration-free location that is free of stray magnetic fields.

For easy use in the field *on magnetic substrates*, a variety of less precise but convenient hand-held magnetic-type instruments are available. Typical of these is the Elcometer, which incorporates a strong permanent magnet and utilizes the magnetic flux across an air gap in the instrument as a measure of the proximity of its probe feet to a ferrous surface. A pointer attached to an armature in the air gap responds to the changes in the magnetic flux with changing distance, thus indicating the thickness of the interposed coating on a direct-reading calibrated scale.

On nonmagnetic metal substrates, electronic instruments operating on the "eddy current" principle can be used to measure dry coating thickness. Such instruments depend on the effect which the conductive base metal exerts on the inductance of a probe coil connected into a suitable electronic sensing circuit. The magnitude of the inductive effect depends on the distance between the coil and the metal and is therefore also related to the thickness of the intervening coating, as given by a calibration curve generated from measurements on standard panels of similar substrate material and known coating thickness. An early instrument of this type, the Filmeter [106], senses the inductive effect on the probe coil as a change in the frequency of an associated oscillator circuit, as measured by restoring the original frequency through "zero-beating" against a fixed reference oscillator. A dial reading corresponding to the frequency change is converted to film thickness by use of a calibration chart furnished with the instrument together with reference panels of known thickness.

Improved instruments based on the eddy cur-

rent principle are now available which greatly simplify the above type of measurement while extending the range, speed, and precision of the measurements. Typical of these are the Boonton, Dermitron, Elcotector, and Permascope instruments. They indicate the magnitude of the inductive effect related to the coating thickness in terms of an immediate meter reading which is readily converted to film thickness by the use of known thickness standards and a calibration chart; or, the meter scale may be calibrated in terms of known thickness standards to give direct readings of coating thickness. While these modern instruments have not yet been incorporated into the body of standard test methods, evaluative work now in progress points to their early adoption in this respect.

It should be noted that although the eddy current-type instruments were designed especially to meet the need for a nondestructive method for measuring the thickness of organic coatings on nonmagnetic metal substrates, this does not preclude their use on magnetic substrates or any other type of electrically conductive substrate.

7.2.2.2. DRYING TIME.—The time required for a freshly applied coating to dry sufficiently to permit satisfactory recoating and placement into service varies widely with the type of coating and with the prevailing atmospheric conditions. It depends also on the thickness and number of coats in the coating system and on the severity of the intended service environment. For example, under favorable atmospheric conditions, the drying time between coats may vary from one hour for a latex paint to 48 hours for an oil-base paint; however, considerably longer drying times may be required for these same materials under conditions of high humidity, low temperature, or poor air circulation. A five-coat paint system would normally require a longer drying time between coats than a three-coat system. Coatings destined for severe exposure in corrosive or abrasive environments should be more thoroughly cured before being placed into service than coatings that are to serve under mild conditions. In cases—contrary to usual practice—where quick-drying coatings containing strong solvents are to be applied over slow-curing coatings (e.g., when a phenolic topcoat is to be applied over an oil-base primer), it is essential that the undercoat be allowed enough additional drying time to assure a thorough cure in order to avoid wrinkling or lifting by the topcoat.

While it is apparent from the foregoing that absolute requirements for drying time cannot be laid down, general guidance is usually provided in the applicable paint specifications, on manufacturers' labels, and by the criteria for

stages of drying (dry-hard, dry-through, etc.) defined in Method 4061 of Federal Test Method Standard No. 141 and elsewhere. The nominal minimum times for recoating specified in the Federal Specifications for various organic coating materials may be seen from the tabular summary presented in chapter 8.

While an adequate drying period between successive coats of paint is essential, excessively long periods of drying between coats of a multicoat system are undesirable because the exposed surface may become contaminated or the coating may cure to a very hard film with adverse effects upon intercoat adhesion.

7.2.2.3. COATING SYSTEM COMPATIBILITY.—A compatible coating system is one in which each applied coat contributes to the over-all performance capability of the system by bonding properly to the substrate or coating beneath it without the development of adverse effects such as lifting, wrinkling, mottling, bleeding, etc. Compatibility, in this sense, begins with consideration of the nature and condition of the substrate and the selection of a suitable primer coating that will have good adhesion to both the substrate and to the topcoat while providing the particular functional properties needed on the given substrate (e.g., sealing of wood or masonry surfaces, wetting and corrosion-inhibition of metal surfaces, and so on —as described in detail in those sections of this volume dealing with coating systems for each important type of substrate (chapter 4). Intermediate and finish coats should be of a type that will wet (and perhaps slightly attack) the preceding coats to ensure good adhesion without the development of the aforementioned film defects.

As a general rule, compatibility of a multicoat system can be assured by using basically the same chemical type of coating material throughout when practicable. For example, if the nature and condition of the surface have dictated the choice of an oil-base primer (as might be the case on hand-cleaned steel), then it would be good practice to use oil-base intermediate and finish coats, provided the latter would meet the exposure requirements. On clean, sandblasted steel permitting the use of a fast-drying oleoresinous primer, compatibility could be assured by using oleoresinous-type intermediate and finish coats. An all-latex paint system would be a compatible coating system for masonry. The principle involved in all these cases is to achieve approximately the same kind of drying behavior, solvent action, solvent resistance, and chemical nature in each part of the coating system to minimize the risk of incompatibility. Other examples may be given: Lacquers normally should be applied only over other lacquers, since they contain strong solvents that would severely attack oil-base, oleoresinous, and various other types of coatings. Many coating systems based on synthetic resins, such as vinyls, neoprenes, epoxies, polyesters, and others, depend upon special primers for the development of good adhesion to the substrate and require close adherence to the manufacturer's recommendations regarding materials and procedures to obtain a compatible coating system capable of maximum performance.

Under some conditions it may not be practicable or desirable to adhere to the general rule of using basically similar materials throughout the coating system. Such might be the case, for example, when incompletely cleaned steel requiring an oil-base primer must serve in a severe environment involving high humidity and water immersion conditions for which an oil-base topcoat would not be suitable. In such cases, the broad principle of compatibility outlined above can still be applied with successful results by selecting a coating system in which there is a progressive transition in properties from inner to outer coats. In the above example of conflicting requirements between primer and finish coats, satisfactory results could be achieved by following the oil-base primer with an alkyd varnish base intermediate coat and finishing with a phenolic varnish-base topcoat, provided sufficient additional drying time for thorough curing were allowed between each applied coat.

An exception to the general rule of choosing chemically similar materials for multicoat systems occurs in cases where a dark undercoat may attack or be attacked by a chemically similar light-colored topcoat, resulting in bleeding of dark material into the light coating. In such cases, the remedy is to use a topcoat sufficiently different in chemical nature that it will not interact with the undercoat. For example, an asphaltic coating will bleed into an oleoresinous topcoat (both being hydrocarbon in nature) when the asphalt is attacked by the hydrocarbon solvents in the oleoresinous coating at the time it is applied; later, the asphalt may continue to attack and slowly migrate (bleed) into the oleoresinous topcoat. On the other hand, a shellac varnish based on an alcohol solvent may be applied over asphalt without danger of lifting or bleeding either at the time of application or later. When employing different types of materials in the same system, care must be taken to ensure adequate intercoat adhesion. Materials too widely different in chemical nature will not bond properly to each other, and the coating system may delaminate when placed into service.

A mixed coating system is desirable also in cases where the substrate contains extractable matter which may bleed into the applied paint. For example, it is not feasible to apply some latex paints directly on redwood because the

water in the paint may extract soluble colored matter from the wood and cause staining of light topcoats. If an oil-base primer is first applied to the redwood, however, to provide a barrier against water-extractable stains, then latex-type finish paints may be used satisfactorily.

In short, compatibility is generally favored by employing chemically similar vehicles in each part of the coating system; however, certain types of different coatings may be intermixed when required, if precautions are taken to ensure compatibility.

7.2.2.4. WORKMANSHIP AND GENERAL APPEARANCE.—A coating system that has been carefully selected to meet the needs of a particular application deserves the careful workmanship necessary to ensure its full performance capability. Shoddy workmanship can spoil both the appearance and the service performance of even the finest coating materials. Adequate time, skill, and care must be given to every aspect of coatings application, from preparation of the surface to application and cure of the final finish coat. Workmen should not only be skilled and conscientious but should also be experienced in the use of the particular coating materials which they are applying. Even basically skilled personnel need instruction and training in the use of new or unfamiliar materials requiring unusual techniques or precautions before they can be expected to do a good job in the field.

Good workmanship begins with the realization that high quality in materials is not a substitute for high quality in workmanship, and vice versa. Nor does skill in using the tools of his trade give the workman the knowledge or right to alter a carefully designed paint formulation by thinning or mixing on the job in any manner except that recommended in the applicable specification or by the coatings manufacturer. Indiscriminate thinning or mixing of materials on the job may later result in a poor appearance or impaired performance even when no outright incompatibility is noticed at the time of the thinning or mixing.

A properly applied coating should cover the substrate uniformly and present a neat, uniform appearance, free from runs, sags, ridges, lap marks, unnecessary brush marks, or other evidences of faulty workmanship. There should be no pinholes, holidays, mottling, blush, cratering, dusting, orange peel, or other signs of unfavorable application conditions, improper thinning, or incorrect formulation. The finished paint job should show no gouges, scratches, thumb or finger prints, embedded dirt, or other marks of carelessness.

Good workmanship is fostered by neat work habits and a concientious attitude which assure the proper care of tools and equipment,

avoidance of the waste and unsightliness of drips and spillage, and protection of adjacent or nearby surfaces and objects by the use of drop cloths or masking tape as needed.

Finally, the essence of good workmanship in painting may be epitomized in the instruction to mix thoroughly, thin properly, and apply uniformly at the recommended spreading rate.

7.2.3. Application of Corrosion-Inhibitive Primers

Information concerning corrosion-inhibiting pigments and primers has been given at several places in the text. The pigments themselves and the manner in which they function were described in section 2.3.1.5. Their formulation into primers for various metals was discussed in section 2.4.2, and their role in the composite coating system was indicated in the discussion of Coating Systems for Metals given in section 4.3 and its various subsections. The theory of corrosion was considered in the introductory portion of section 4.3, wherein the galvanic nature of the corrosion process was pointed out. It remains now to point out certain important principles which must be borne in mind in the application of corrosion-inhibitive primers.

When applying corrosion-inhibitive primers to metal surfaces, it is essential that the entire surface area be coated. Otherwise, the corrosion at small, localized uncoated areas (pinholes and holidays) may be intensified far beyond that which would have occurred without any coating at all. The reason for this lies in the galvanic or electrochemical nature of the corrosion process. Differences in electrical potential arising between dissimilar metals or dissimilar areas in or around the same metal cause a flow of electric current that dissolves away the anodic (corrodible) material while affording protection to the cathodic material. If the anodic areas are very small compared to the cathodic area, all the current which flows will be concentrated at these small anodic areas and they will rapidly become deeply pitted or perforated.

As an example, consider the case of a brass valve connected between lengths of steel pipe. The steel pipe, being anodic to the brass, will corrode while protecting the brass. If one should be tempted to apply a protective coating only to the corroding steel pipe, a situation could arise in which a pinhole in the pipe coating would become the anode for all the galvanic current furnished by the much larger brass cathode, and perforation of the pipe would soon result. The best way to avoid such a potentially disastrous corrosion situation is to paint both the anodic and the cathodic surfaces.

While the above principles have been pre-

sented in terms of a coating system employing a corrosion-inhibiting primer because of the general use of such primers on metal exposed to corrosive environments, the principles are equally applicable to any barrier coating applied to a metal substrate.

7.2.4. Helpful Hints

The following is a collection of miscellaneous helpful hints and useful facts not given or not emphasized elsewhere in this publication.

7.2.4.1. WETTING PROPERTIES OF COMMON COATINGS.—Among the oil-base, oleoresinous, and vinyl coatings that have proved widely useful for the protection of steel (see sec. 4.3.1) there is a progressive increase in resistance to corrosive environments (and, happily, in drying speed) as one progresses from straight oil-base vehicles to alkyd-base vehicles to phenolic-base vehicles to vinyls. Unforunately, this progressive, advantageous increase in corrosion resistance is offset by a progressive decrease in the surface-wetting ability of these vehicles. Thus, the oil-base vehicles which are the least resistant to corrosive environments are the slowest drying and have the best wetting properties, whereas the vinyl vehicles which are the most corrosion-resistant and most rapid drying have the poorest wetting ability. The lower the wetting ability of the paint, the more thorough must be the surface preparation to ensure adequate adhesion and durability. While one should always select a coating system which will have adequate durability in the environment to which it is to be exposed, it is obviously uneconomical to apply the more corrosion-resistant coating systems in mild environments where the expense of extra surface preparation necessitated by their lower wetting ability cannot be justified on the basis of increased service life.

7.2.4.2. SOURCES OF SPECIFICATIONS.—Some uncertainty and confusion exist regarding procurement sources of Government and other specifications. The following is presented as a general guide.

7.2.4.2.1. *Federal Specifications* are prepared under the direction of the Administrator of General Services by appropriate technical agencies of the Government and are promulgated by the Administrator. All Federal Specifications, including interim specifications, are listed in the Index of Federal Specifications, Standards, and Handbooks [67] which is prepared by the General Services Administration of the Federal Supply Service. Government activities should obtain copies of this Index and the periodic cumulative supplements through departmental channels where established, or

by forwarding a purchase order to the Specifications Activity, Printed Materials Supply Division, Building 197, Naval Weapons Plant, Washington, D.C. 20407. Non-government activities may purchase copies of the Index from the Superintendent of Documents, U. S. Government Printing Office, Washington, D.C. 20402. The specifications and other documents listed in the Index must be obtained, however, from the Specifications Activity identified above. Single copies of product specifications required for bidding purposes may be obtained without charge from GSA Business Service Centers serving regional areas in various parts of the country, as identified in the Index of Federal Specifications. A quick guide to and summary of Federal Specifications for organic coating materials are given in chapter 8.

7.2.4.2.2. *Military Specifications* are listed in the Department of Defense Index of Specifications and Standards [68] which is for sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. The specifications and other documents listed in the Index are available to qualified activities on request from the Commanding Officer, Naval Supply Depot, 5801 Tabor Avenue, Philadelphia, Pennsylvania, Attn: Code CDS. Specific references to a selected group of Military Specifications for organic coating materials are given in the bibliography of Chapter 9.

7.2.4.2.3. *Federal Test Methods* for organic coating materials are compiled in *Federal Test Method Standard No. 141 for Paint, Varnish, Lacquer, and Related Materials; Methods of Inspection, Sampling, and Testing* which may be purchased from General Services Administration, Business Service Center, Washington, D.C. 20405, for approximately $3.00 each.

7.2.4.2.4. *ASTM Test Methods* may be purchased by Government activities through the Federal Supply Schedule (FSC Group 76, Part I, Item No. 36-1). Nongovernment activities may purchase them directly from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.

7.2.4.2.5. *ASA Standards** may be purchased by both Government and nongovernment activities directly from the American Standards Association, Inc., 10 East 40th Street, New York, New York 10016.

7.2.4.3. APPLICATION HINTS (also see sec. 4.1.5).

7.2.4.3.1. *When applying multicoat paint systems,* the use of a contrasting shade or color for

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* Now called USASI Standards, since the name of the American Standards Association was recently changed to United States of America Standards Institute.

successive coats will provide visual help in assuring the uniform and adequate application of each coat.

7.2.4.3.2. *When painting metal*, care must be exercised to avoid leaving any exposed metal or holidays which could become focal points for the start and spread of corrosion. Inadvertent exposure of bare metal or inadequate paint thickness is most likely to occur in difficult paint-holding areas such as sharp edges, rough or unclean welds, sharp prominences, and pits or crevices in the surface. In such cases, careful brush application—particularly of the first or primer coat—generally gives better results than other application methods because it provides an opportunity to work the paint into or onto the irregular surface (see sec. 5.4.1).

7.2.4.3.3. *When applying latex paints*, it should be remembered that while these may be applied without difficulty on damp or lightly wet surfaces, they should not be applied to water-soaked surfaces or to substrates containing large amounts of internal moisture, such as fresh concrete or fresh plaster. Normally, at least 4 weeks of drying is desirable before painting the latter surfaces, to allow for a reduction of the free moisture and excessive alkalinity. Under exceptional circumstances, this drying time may be reduced to only two weeks before applying a first coat of latex paint or primer-sealer, provided that application of the topcoat is deferred until the primed plaster or concrete has dried sufficiently by diffusion of moisture through the still-permeable first coat. The application of latex paints has been discussed at several places in the text, including sections 2.3.5.3, 2.4.3, 2.4.4, 4.4.3, 4.5, 6.4, 6.5.1, and 7.2.1.

7.2.4.3.4. *Vinyl coating systems* for the protection of steel under severely corrosive conditions in industrial or marine environments depend upon special primers for the development of maximum adhesion and corrosion resistance. The most widely used primer for this purpose is a vinyl-red lead type such as that described by Military Specification MIL–P–15929. A zinc chromate-vinyl type primer such as that described by Military Specification MIL–P–15930 also may be used. It must be emphasized that both of these primers *require* the use of a vinyl wash primer or washcoat pretreatment such as that described by Military Specification MIL–C–15328 (see secs. 4.3.1.2 and 6.3.2.5).

7.2.5 Test Equipment and Test Methods

The subjects of TEST EQUIPMENT AND TEST METHODS cover a broad field which (with the exception noted below) is beyond the scope of the present volume. For information on these subjects reference should be made to standard works such as the Gardner Paint Test Manual [98], the Book of ASTM Standards, Federal Test Method Standard No. 141, and the works of Mattiello. Information is given also in the books by Payne, by von Fischer, by Burns and Bradley, and by others listed in the General Bibliography of chapter 9. This manual does, however, present information on methods for measuring thickness, as an integral part of the discussion of coating thickness requirements given in section 7.2.2.1.

7.2.6. Paint Film Defects and Failures

Paint film defects and failures are beyond the scope of this volume. This subject has been covered in depth by Hess [107] and in the work of the Research Committee of the Federation of Paint, Varnish, and Production Clubs [108]. The subject also has been considered by Chatfield [109] and others, and in a number of articles in the literature. Definitions and pictorial examples of specific types of failure (e.g., blistering) may be found among the Standards of the American Society for Testing and Materials (see General Bibliography). Good pictorial examples of paint failures on wood surfaces are given in the paint manual of the Corps of Engineers [41] and in the older National Bureau of Standards Paint Manual [110] which is superseded by the present publication.

7.2.7. Basic Information

As part of the consolidation of information which is a prime objective of the present chapter, it may be useful and appropriate to list—apart from the Index or the Table of Contents—specific sections in the text where important fundamental or basic information is given:

Subject	Section
NATURE of:	
Organic coatings	2.1
Drying oils	2.2.1
Primers	2.4
FORMULATION of:	
Strippable coatings	2.2.7
Latex paints	2.3.5.4
Multicolor finishes	2.3.7
Fire-retardant coatings	2.3.8.1, .2, .3
Textured coatings	4.1.4.5
FUNCTION of:	
Pigments in paint	2.3.1.1, .3, .5
Functional coatings	4.6
POLYMERS:	
Polymeric nature of synthetic resins	3.1
Relation between polymer structure and properties	3.1.1
The functionality concept in polymerization	3.1.2
Methods of polymerization	3.1.3
Types of polymers according to structure	3.1.4
Classification of synthetic resins	3.1.5

7.3. Use of the Text to Solve Specific Coating Problems

The following sections are intended to illustrate the usefulness of the monograph in solving coating problems by indicating suitable coating systems for a variety of typical applications, together with specific cross-references to the places in the text where this information can be found. The examples given serve the dual purpose of furnishing specific solutions to typical coating problems while providing an insight into effective utilization of the information contained in the text.

It should be emphasized that the recommendations made, while assuring a suitable coating system for the intended application, do not preclude appropriate modifications or the use of other types of coating systems which may be equally suitable. The examples given are typical and illustrative rather than unique solutions to the problem at hand.

Before considering specific solutions, it will be helpful to review the general approach to the problem of coatings selection which is given in the introduction and section 4.1 of chapter 4. The examples to be given represent the practical application of those basic principles.

In using the text, the information on selection of coating systems will be found in chapter 4, application methods are described in chapter 5, and surface preparation is covered in chapter 6. In all painting operations, the safety precautions emphasized in section 5.2 should be kept in mind and adhered to. A quick guide to and summary of Federal Specifications referred to is given in chapter 8.

In the examples which follow, all the information given may be found in the text, as indicated by appropriate cross-references to specific sections in the text.

7.3.1. Example No. 1:
Selection and Application of a Suitable Coating System for New Exterior Wood Siding on a Home in an Ordinary Urban Environment

Wood surfaces require the use of a primer or undercoater for best results (4.2). For exterior use, a specially formulated oil or oleoresinous type such as that described in section 2.4.1 and typified by Federal Specification TT–P–25 is highly desirable. The undercoat should be followed by one or preferably two topcoats of a linseed oil paint (4.2.1). Reference to the Quick Guide to Federal Specifica-

tions (sec. 8.1.3) reveals a half dozen oil-base paints. Further reference to the summary chart of Federal Specifications (sec. 8.2) and a glance down the "for use on wood" column leads to three exterior oil paints for wood, among which TT–P–102 is seen to be appropriate for general use in ordinary environments.

The wood surface should be clean and dry when the paint is applied; prepare the surface in the manner described in section 6.2.1. Application by brush (5.4.1) is preferred (see "application method" column in summary charts of section 8.2). The painting should be done in favorable weather (7.2.1). The undercoat should be applied at a spreading rate of about 450 square feet per gallon and the topcoats at about 650 square feet per gallon to yield an over-all dry film thickness of 4 to 5 mils (7.2.2.1). A drying time of 48 hours should be allowed between each coat, as mentioned in section 7.2.2.2 and as specifically indicated in the summary chart (8.2) for Fed. Spec. TT–P–102. The paint should be applied in a workmanlike manner that produces a good final appearance (7.2.2.4).

NOTE: To avoid unnecessary repetition, the copious cross-references provided in this first example are not repeated in such detail in subsequent examples.

7.3.2. Example No. 2:
Selection and Application of a Coating System for Structural Steel to be Exposed in a Moderate Industrial Environment

A satisfactory coating system for steel begins with the application of a suitable corrosion-inhibiting primer to the clean metal (4.3). Exposure in a moderate industrial environment suggests the use of an alkyd resin-base system, which is intermediate in durability between a straight oil-base system (for mild exposure) and a phenolic resin system (for severe exposure under conditions of condensation or fresh water immersion). To ensure a compatible system (7.2.2.3), it is normally desirable that the alkyd-base topcoat be applied over an alkyd varnish-base primer. The latter requires smooth, thoroughly clean steel for the development of adequate adhesion, as would be obtained by sandblasting to "white metal" (6.3.1.8.1). Assuming that only "brush-off" blast cleaning (6.3.1.8.4) or power tool cleaning (6.3.1.7) is feasible in this instance, the

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choice of a suitable primer is narrowed to either an oil-base type or a raw linseed oil-fortified, long oil-alkyd type, with the latter preferred because of its better resistance and its better compatibility with the alkyd topcoat to be employed. All the foregoing information is contained in section 4.3.1.1, which also indicates that suitable primers having this general composition are covered by Federal Specifications TT–P–86, Type II or TT–P–57, Type I. Reference to the summary chart of section 8.2 also indicates the composition of these primers, and further reveals that the TT–P–86, Type II primer is somewhat faster-drying than the TT–P–57, Type I primer. Assuming that the TT–P–86 primer is selected for its faster drying and because of the proven performance of red lead-type primers, it is desirable that the 16-hour nominal drying time given in the chart be increased to at least 24 hours to ensure compatibility with the alkyd-base topcoat to be applied. A high quality alkyd gloss enamel suitable for the topcoat is described by Federal Specification TT–E–489, as indicated under "Intermediate and Finish Coats" in section 4.3.1.1.1.

7.3.3. Example No. 3:
Selection and Application of a Coating System for Galvanized Steel to be Exposed in an Ordinary Environment

Galvanized steel that is well-weathered and free of rust, oil, or dirt can be coated with conventional paints without undue difficulty, but the use of a zinc dust primer such as that covered by Federal Specification TT–P–641 is recommended (4.3.1.4). In this instance the Type II material, based on a long-oil, linseed-modified, alkyd resin vehicle provides a good combination of wetting properties, drying time (nominally 18 hours as indicated in the summary chart for TT–P–641 in section 8.2), and durability. New galvanized steel must be thoroughly washed with solvent (6.3.1.1) to remove processing contaminants from the surface. If it is known that the galvanized steel has not received a factory chromate treatment (6.3.3.1), best results will be obtained by use of a cold zinc phosphate pretreatment of the brush-on or wash type (6.3.2.2) or by applying a wash primer type pretreatment coating (6.3.2.5), before applying the zinc dust primer. The type TT–P–641 material may also be used as the topcoat in this system.

7.3.4. Example No. 4:
Selection of a Coating System for the Inside of a Potable-Water Tank

For the protection of potable water tanks, section 4.3.1.1 recommends the use of a zinc dust-pigmented primer and paint based on a

suitable (non-toxic) phenolic varnish vehicle. Such a paint is covered by Military Specification MIL–P–15145 (Formula No. 102).

7.3.5. Example No. 5:
Selection and Application of a Coating for a Cinder-Block Basement Wall

Select a cement-water paint of the desired color (secs. 2.3.9.1 and 4.4). The surface should not previously have been painted with an organic coating and should be free of chalky or crumbling, old cement paint (6.6.4.3); otherwise, it must be prepared by power wire-brushing to remove all the old coating. Dampen the surface before applying the cement-water paint, and keep the surface damp while the coating cures, especially for the first 48 hours (4.4.1). A cement water-paint, properly-applied and cured, provides a very durable finish that is permeable to moisture but unaffected by dampness or alkalinity. Federal Specification TT–P–21 covers a cement-water paint (located by reference to "quick guide" in section 8.1.3), with further details in summary chart of 8.2).

7.3.6. Example No. 6:
Selection and Application of a Coating System for Exterior Concrete

A latex paint system is suitable for application to a properly prepared exterior concrete surface (4.4). Either an acrylic type such as that covered by Federal Specification TT–P–19 (see summary chart, sec. 8.2) or a polyvinyl acetate type such as that conforming to Federal Specification TT–P–55 may be used. The concrete should be allowed to age as long as practicable, but not less than 30 days, before painting (6.4.1). The surface should be cleaned free of dirt, curing compounds, loose chalk, and other foreign matter by the methods described in section 6.4.2. Efflorescence, if present, must be completely removed—by sandblasting (6.3.1.8) when feasible; otherwise, by treatment with dilute muriatic (hydrochloric) acid. A primer coat (usually simply a thinned version of the topcoat) should be applied to the clean surface, followed by one or two coats of the unthinned topcoat material (2.4.3 and 4.4.3). It is usually advantageous to dampen the concrete surface before applying the primer or primer-sealer (2.4.3, 7.2.1, and 7.2.4.3.3). Drying time between coats need be only an hour or two in clear, dry weather (summary chart, 8.2).

7.3.7. Example No. 7:
Coating System for Gypsum Wallboard (Dry Wall)

Section 4.5 indicates that a latex system is suitable for use on gypsum wallboard and

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recommends use of a latex primer-sealer such as that covered by Federal Specification TT–P–650 to avoid raising the nap of the outer paper layer. The primer-sealer may be followed with a topcoat of latex paint conforming to Fed. Spec. TT–P–29. Alternatively, oil-base or alkyd-base paints may be applied over the latex primer-sealer.

7.3.8. Example No. 8:
Selection and Application of a Coating System for Aluminum Exposed to a Moderately Corrosive Atmosphere

Solvent-clean the surface to remove all oil, grease, and soil (6.3.1.1). Pretreat the surface with wash primer such as that conforming to Military Specification MIL–C–15328 in the manner prescribed in section 6.3.2.5. Follow with a zinc yellow primer (6.3.4) such as that covered by Fed. Spec. TT–P–666. The zinc chromate primer may be over-coated with any one of a wide variety of coatings, including oil-base or oleoresinous types, vinyls, epoxies, cellulose esters, etc., as indicated in section 4.3.3 and as described in chapter 3.

7.3.9. Example No. 9:
Coating for Wooden Gymnasium Floor

A polymeric finish such as a polyurethane or an epoxy coating will provide excellent durability in a severe service application such as a gymnasium floor, bowling alley, or areas of heavy foot traffic (4.2.2). Epoxy-polyamide coatings also provide good durability in such applications. A conventional floor varnish of moderate durability is covered by Fed. Spec. TT–V–71 (see summary chart, sec. 8.2).

7.3.10. Example No. 10:
Acid-Resistant Coating

Consult section 4.6 which indicates outstanding materials for specific functional purposes. Acid-resistant coatings are named in section 4.6.1.1. Possible choices are (1) polyvinyl chloride coating for resistance to all except strong oxidizing acids, and (2) chlorinated rubber coating for resistance even to strong oxidizing acids. If required, even greater acid resistance could be obtained with coatings such as polytetrafluoroethylene or cholorotrifluoroethylene.

7.3.11. Example No. 11:
Fire-Retardant Coating System

The function, performance capability, and classification of fire-retardant coatings are discussed in section 2.3.8. A basis for their selection is given in section 2.3.8.5, wherein reference is made to a number of Federal and Miliary Specifications for fire-retardant coatings (see Bibliography, references 19 through 24).

7.4. Summary and Conclusion

Preceding chapters of this publication have described its objectives and arrangement, discussed the early history of paint and varnish, described the types of coatings that are available, given the properties and uses of all the important synthetic resins available today, provided a basis for their selection, and given information on application methods, surface preparation, and pretreatment.

The present chapter consolidates the information given and presents important supplementary information.

The two remaining chapters present a quick guide and a summary of Federal Specifications for organic coating materials, and a selected bibliography of works in the coatings field.

While the monograph has endeavored to be a comprehensive guide rather than a specific directive for the use of organic coatings, much of the information presented may be the basis for such instructions, particularly where the newer materials are to be utilized.

It is hoped that the publication will serve as a comprehensive, unifying treatise in the field of organic coatings.

FIGURE 7.1. *Eddy-current thickness gage for nondestructive measurement of thickness of nonconductive coatings on metal substrates, as described in ASTM Method D 1400-67T. (See text, p. 138.)*
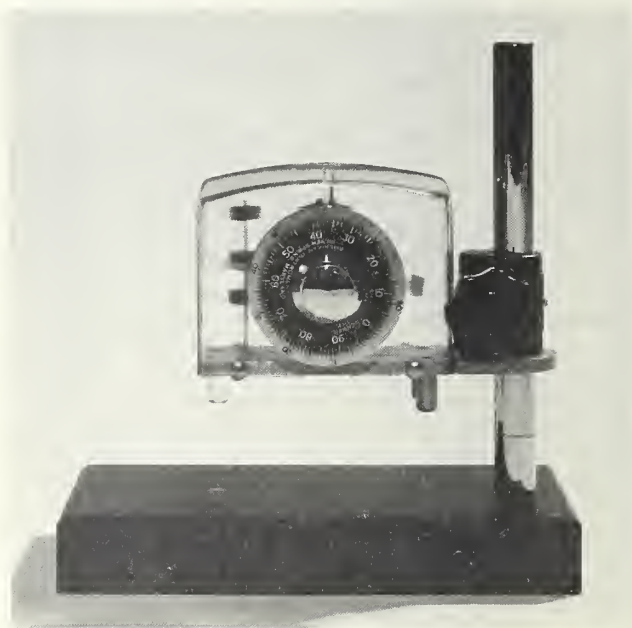
FIGURE 7.2. *Magne-Gage measures thickness of nonmagnetic coatings on magnetic (ferrous) substrates (see text, p. 138) as described in ASTM Method D 1186-53.*
(Photo courtesy of American Instrument Co.)
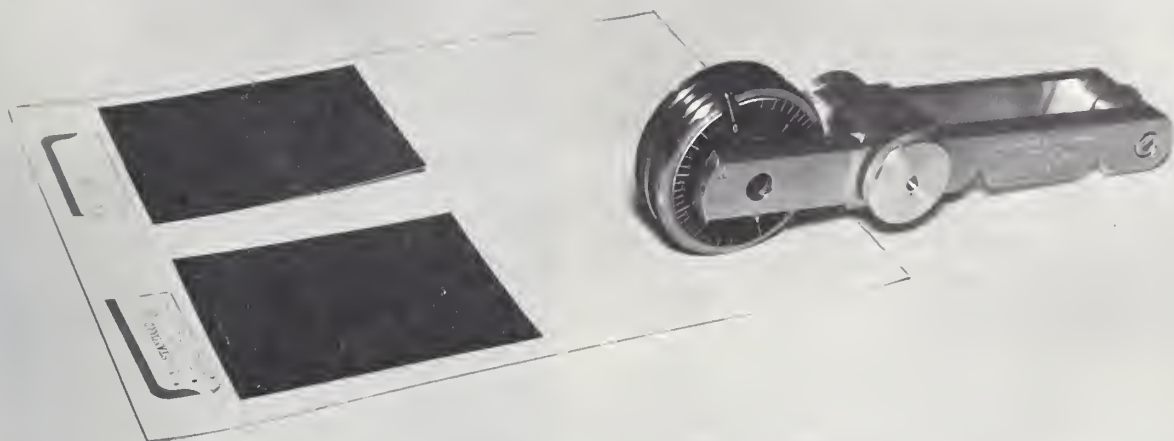
FIGURE 7.3. *Interchemical wet film thickness gage, with holder; when gage is rolled over wet surface, thickness is indicated by point of first contact of paint with recessed, eccentric, calibrated inner wheel, as described in ASTM Method D 1212-54 (also, see text, p. 137).*
(Photo courtesy of Gardner Laboratory.)
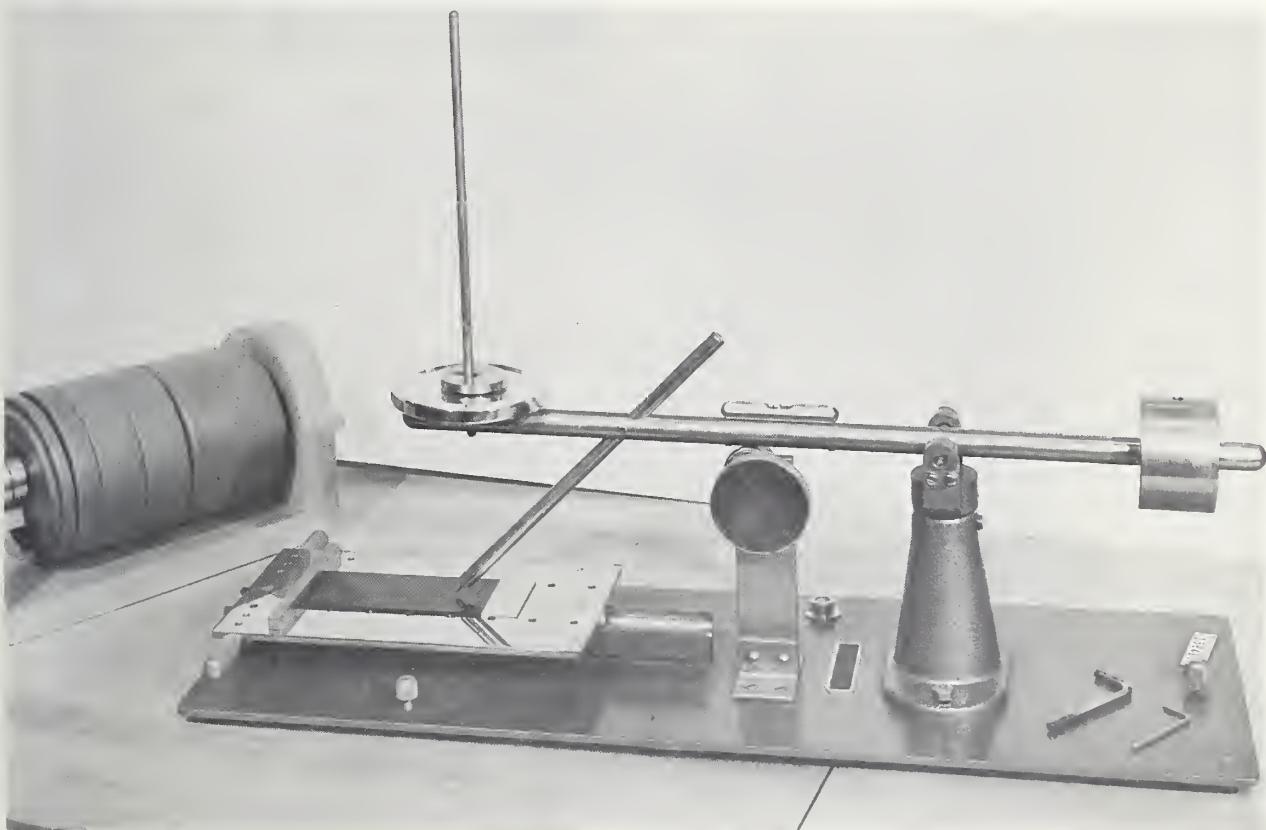
FIGURE 7.4. *Balanced-beam scrape-adhesion tester determines load required to remove coating with U-shaped stylus, as described in ASTM Method D 2197-63T.*

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FIGURE 7.5. *Pfund hardness tester measures diameter of indentation produced by a hemispherical sapphire indenter under a specified load, as described in ASTM Method D 1474-62T.*
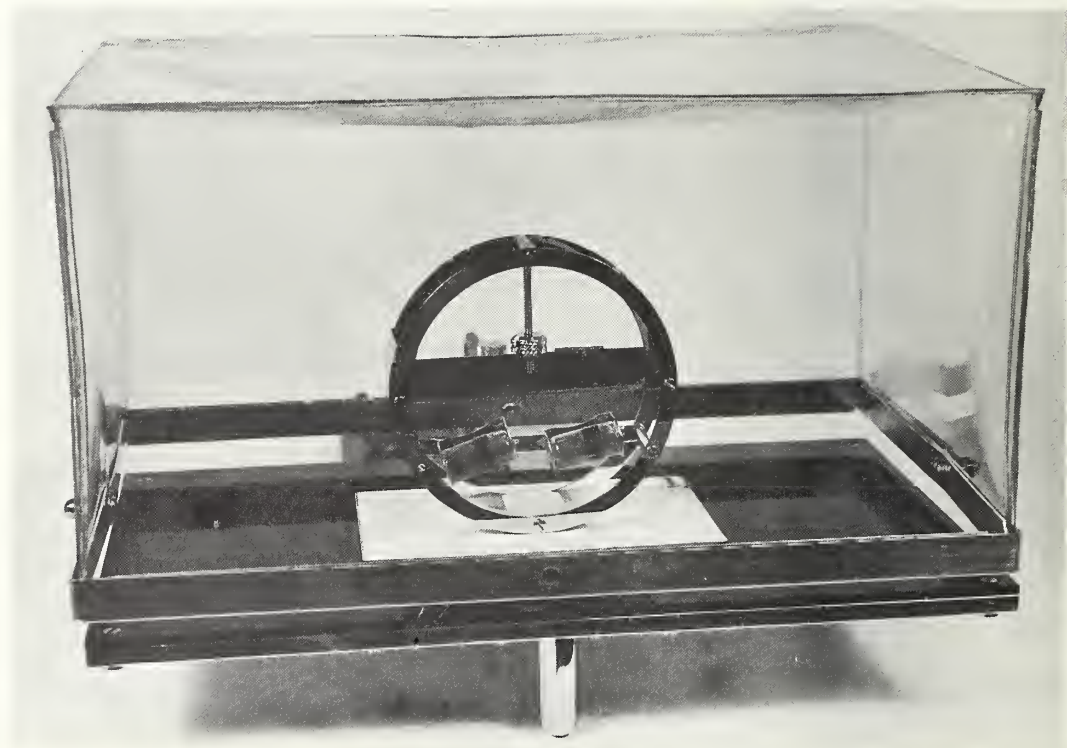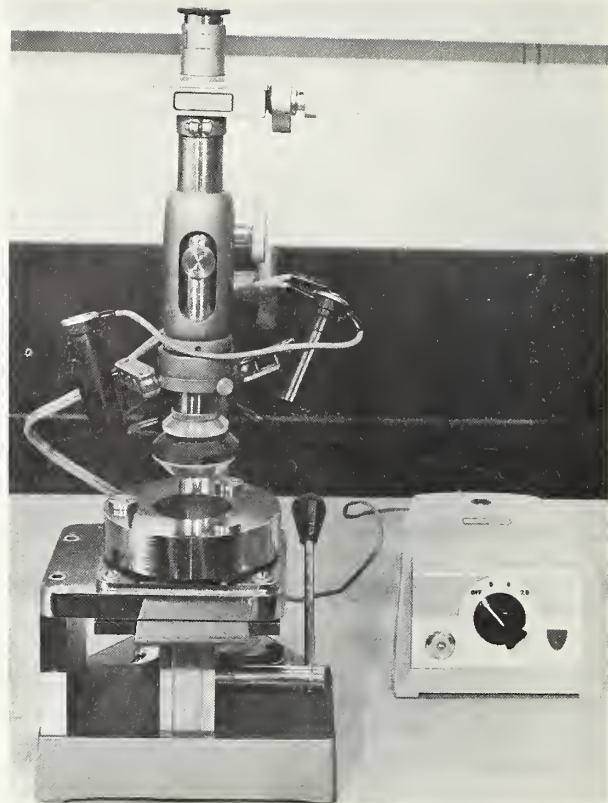
FIGURE 7.6. *Sward hardness rocker; the harder the surface, the greater the number of swings obtained before the rocking amplitude decays to a specified level.*
(Photo courtesy of Gardner Laboratory.)

8. Summary of Federal Specifications for Organic Coatings

This chapter presents a concise summary of important Federal specifications for organic coating materials in the form of two complementary tables. The first is a list of letter-number designations of Federal specifications classified according to generic type and use for quick, convenient reference. While this table is complete, at this writing, with respect to organic coatings, the listing of accessory materials is limited to a few of the more important thinners, paint removers, and other auxiliary items. In addition to being more convenient and informative than a straight alphabetic or numerical listing, the classified list provides an entree to the more comprehensive tabular summary which follows it.

The second table offers a compendium of the essential technical information contained in a selected list of important Federal specifications for organic coatings. The concise tabular arrangement provides a rapid and convenient means for obtaining at a glance the key information in a given specification, or for finding a Federal specification for a coating material to meet the needs of a particular application.

8.1. Quick Guide to Federal Specifications for Organic Coating Materials

The following list gives only letter-number designations[1] of Federal specifications, but it groups them under generic headings that facilitate the finding of a particular type of material. The full titles of these specifications may be found in the Index of Federal Specifications [67]. More comprehensive information about many of these materials can be found in the tabular summary of important Federal specifications which follows the classified list.

8.1.1. Enamels

ALKYD—Gloss: E–489, E–491, E–505, E–560
    Semi-gloss: E–485, E–509, E–529
    Lustreless: E–527
    Rust-inhibiting: E–485
    Heat-resistant: E–496
    Undercoat: E–543, E–545

Floor and deck: E–487

8.1.2. Lacquers

Acid-resistant: L–54

Cellulose nitrate: L–26, L–31, L–40

Cellulose nitrate-Acrylic: L–50 (aerosol type)

Multicolor: L–45

Rubbing: L–57

Spraying (general purpose): L–58

8.1.3. Paints

Alkyd, flat: P–30

Alkyd resin emulsion: P–18

Cement-water: P–21

Cold water: P–22, P–23

Fire-retardant: P–26, P–34

Heat-resisting: P–28

Iron oxide type: P–31

LATEX—Acrylic: P–19
    Polyvinyl acetate: P–55
    Styrene-butadiene: P–0099
    Type unspecified: P–29

Oil-base (no resin): P–20, P–27, P–61, P–102, P–103, P–104

Oil-alkyd: P–53, P–59, P–71, P–81

Oil-base or Oleoresinous: P–14, P–47, P–51

Oleoresinous emulsion: P–18, P–88

Phosphorescent: P–54

Red-lead-base: P–86

Rubber-base: P–91, P–95

Stencil: P–98

Traffic: P–85, P–0087, P–115

8.1.4. Primers

For Wood: P–25, P–636, P–659

For Ferrous Metals: P–57, P–86, P–615, P–636, P–645, P–659, P–662, P–664

For Aluminum and Magnesium and their Alloys: P–645, P–666

For Galvanized Metal: P–641

For Masonry, Plaster, and Wallboard: P–29, P–30, P–56, P–650

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[1] For the sake of brevity, the prefix "TT—", which applies to all specifications listed, has been omitted.

8.1.5. Sealers

Varnish type: S–176

Lacquer type: S–171, S–190

Sealer and lubricant (for wood): S–180

8.1.6. Stains

Opaque, exterior: S–706

Semi-transparent, exterior: S–708

Interior (oil type): S–711

8.1.7. Varnishes

Asphalt: V–51

Damar: V–61

Mixing (for aluminum paint): V–81

Oleoresinous: V–71

Rubbing: V–86

Shellac: S–300

Spar: V–109, V–119, V–121

8.1.8. Miscellaneous Coatings

Calcimine: C–96

Rust-inhibitive compound: C–530

Strippable: C–517

Surfacer: S–810

Vehicle underbody: C–520

8.1.9. Accessory Materials

Aluminum-pigment powder and paste: P–320

Caulking compound (plastic): C–598

Driers: D–643, D–651

Fillers: F–320, F–336, F–340

Paint Removers: R–230, R–243, R–251

Putty: P–781, P–791

Rubbing Compound: R–771

THINNERS—Dope and lacquer: T–266
Mineral spirits (petroleum): T–291
Mineral spirits (odorless): T–295
Synthetic enamel: T–306
Turpentine: T–801

Notes: (1) For full titles of specifications, or for a straight alphabetic or numerical listing, consult the published Index of Federal Specifications [67].

(2) For more comprehensive information on a selected group of important organic coating materials from the above list, see the tabular summary which follows in Section 8.2 of this chapter.
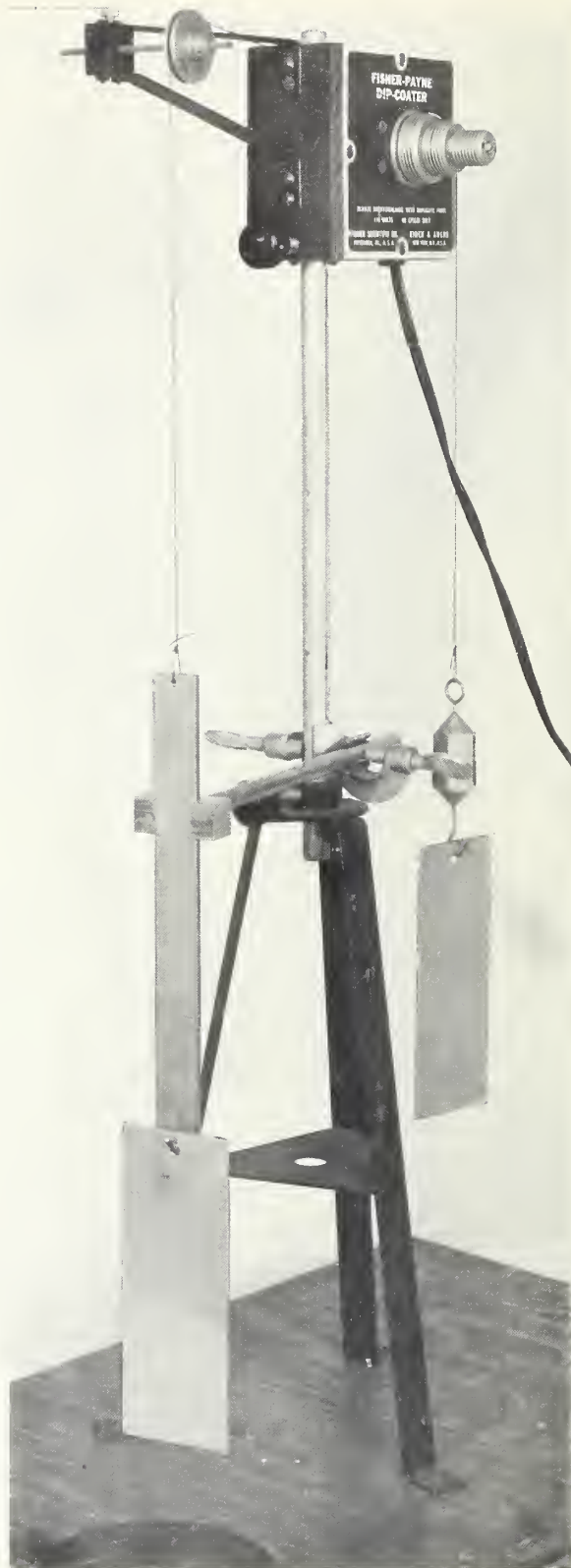
FIGURE 8.1. *Improved dip-coater prevents test panel from turning and scraping against sides of narrow dip tank. (Roberts, A. G., & R. S. Pizer, Improved dip-coater, Anal. Chem. 26, 790, Apr. 1954).*

8.2. Tabular Summary of Important Federal Specifications for Organic Coatings

8.2.1. Description and Use

The tabular summary lists the specifications in sequence by letter and number, so that similar materials are generally grouped together. It will be noted here and in the Index of Federal Specifications [67] that Federal specifications for organic coating materials (e.g., TT–L–31) bear the general group designation "TT", followed by a subgroup letter denoting the general type of coating (for example, E for enamel, L for lacquer, P for paint or primer, etc.) and finally an identifying number. For each specification, there is tabulated a brief description of the material and its basic purpose, the nature of the coating vehicle, information on which surfaces and under what conditions the material is used, the method of application and cure, the drying time, outstanding properties of the material, and notes on its intended use.

Basically, as stated in the introduction to this chapter, the tables may be used either to obtain at a glance the key information contained in a particular specification, or to find a Federal specification for a coating material to meet the requirements of a particular application. More specifically, among the ways in which the tables may be used are the following:

(1) *To identify the material described by a specification for which only the letter-number designation is known, and to give the essential properties and applications of the material.* For example, the table quickly indicates that TT–L–31 describes a cellulose nitrate gloss lacquer, alkyd-resin modified, for use as a weather-resistant protective coating on smooth, clean, exterior metal; also, that the lacquer is applied by spraying and air-dries sufficiently for recoating in six hours, plus other information.

(2) *To find a specification or a type of coating suitable for interior or for exterior use (or both) on a particular type of substrate.* For example, if one needs a coating for interior wallboard, a glance down the "wallboard" column will indicate immediately, by code letter "I", a number of potentially suitable materials from among which a further selection may be made on the basis of the additional information given as to type of coating, nature of vehicle, properties, and use. If, for instance, TT–E–543 is considered, the table indicates further that this is an enamel-type undercoat and that the wallboard must be sealed with a suitable primer-sealer before application of the undercoat.

(3) *To find a specification for a coating intended for a certain type of use,* such as an oil-base paint (house paint), a floor and deck enamel, a spar varnish, a latex paint, a primer for aluminum, a traffic paint, a swimming pool paint, etc. Such coatings can be found readily by scanning the material description blocks in the first column.

(4) *To locate a coating based on a particular type of vehicle,* such as a drying oil, an oleoresin, an alkyd resin, cellulose nirate, polyvinyl acetate, rubber, etc. As in (3), this is readily accomplished by scanning the material description blocks in the first column. These blocks usually list the basic type of vehicle even when this is not given in the formal specification title or in conventional title indexes.

Alternatively, one may locate specifications relating to the purposes of (3) and (4) above by referring to the classified list of specifications given in Section 8.1 of this chapter.

The tabular summary charts are on the following pages.

FIGURE 8.2.   *Modern outdoor exposure racks can be set for any angle in a single longitudinal plane. Hinged cross bars are adjustable to retain specimens of different lengths.*

8.2.2. Quick-Glance Summary Tables

Quick-Glance Summary of Important Federal Specifications for Organic Coating Materials

[a]Specification number and material described	Class or type; nature of resin or vehicle	For use on[b] Wood	Metal	Masonry	Plaster	Wallboard	Application[c] Method	Cure	Drying time	Valuable properties	Notes on intended use
TT–E–485. Alkyd semi-gloss enamel, rust-inhibiting.	[d]Type I: Medium oil (linseed-soya) alkyd.	----	E	----	----	----	D	A / B	16h / 45m	Good resistance to weathering, water, and hydrocarbon fluids. Good flexibility and adhesion.	For use as 1- or 2-coat system over properly cleaned and treated metal, such as sheet metal, ammunition containers, landing mats, pipeline equipment, gasoline drums, vehicles, and rail and marine equipment. In a 2-coat system, first coat may serve as primer.
	[d]Type II: Same as type I.	----	E	----	----	----	BS	A / B	16h / 45m		
	[d]Type III: Same as type I.	----	E	----	----	----	R	A / B	16h / 45m		
	Type IV: Phenol modified alkyd resin.	----	E	----	----	----	BSD	A / B	8h / 45m	Same as above plus ability to flash dry set-to-touch in 4 to 10 minutes.	
TT–E–487. Floor and deck enamel.	Tough and flexible varnish vehicle of high quality, with turpentine or volatile mineral spirits. Free of rosin or rosin derivatives.	IE	----	IE	----	----	B	A	16h	Tough, flexible, and abrasion-resistant. Good drying properties. Good resistance to water.	For wood and concrete basement floors not subject to dampness. Allow concrete to age for one year before painting. Apply in thin layer to dry floor under low humidity conditions. Allow ample drying time between coats.
TT–E–489c. Alkyd gloss enamel.	Class A: Medium oil (linseed-soya) alkyd.	IE	IE	----	----	----	BS	A	8h	Highly weather resistant. Good color and gloss retention. Good drying and freedom from after-tack. Good flexibility.	For primed exterior and interior wood or metal, particularly smooth exterior metal. For finishing or refinishing autos, trucks, construction equipment, metal signs, machinery, metal railing, freight cars, etc. *Not* intended for houses or plastered walls.
	Class B: Short to medium oil alkyd plus 10–20% urea- or melamine-formaldehyde resin.	IE	IE	----	----	----	S	B	45m		
TT–E–505a. Alkyd enamel, high gloss, "odorless", (white and light tints).	Drying oil alkyd (soya), in odorless mineral spirits.	I	I	----	I	I	B	A	12h	Low odor, easy brushing, excellent color retention and flexibility, highly washable, good drying, no after-tack.	For general interior use on primed walls and ceilings of plaster and wallboard, wood trim, and metal. Useful in hospitals, laundries, kitchens, bathrooms, where maintenance of sanitary conditions is important. Also for decorative coating on surfaces indicated.
TT–E–506c. Alkyd gloss enamel (tints and white).	Long oil alkyd (linseed- or soya-modified), in petroleum or terpene thinners.	I	I	----	I	I	B	A	16h	Easy brushing, excellent color retention, good drying, no after-tack, highly washable, excellent flexibility.	For general interior use on primed plaster and wallboard and on suitably prepared wood trim and metal. Particularly useful in hospitals, laundries, kitchens, bathrooms; on walls, ceilings, and woodwork. (Like TT–E–505a, but not odorless.)
TT–E–509a. Alkyd	Drying oil alkyd (soya), in	I	I	----	I	I	B	A	12h	Low odor, easy brush-	For general interior use on primed

Specification	Vehicle (composition)	Use[b]	Method[c]	Cure[c]	Drying Time[c]	Properties	Uses and remarks
semi-gloss enamel, "odorless" (white and tints).	odorless mineral spirits.					ing, excellent color retention and flexibility, good drying, no after-tack, good water and soap resistance.	plaster and wallboard and on suitably prepared wood trim and metal. Very useful in hospitals, laundries, kitchens, bathrooms, where maintenance of sanitary conditions is important; also, for decorative use on properly primed walls, ceilings, and woodwork.
TT-E-527a. Alkyd lustreless enamel.	Medium drying-oil phthalic alkyd (typically, linseed-soya modified); free from rosin or phenolic resin.	E / E	BS / BS	A / B	8h / 45m	Good resistance to weathering, polishing, water, and hydrocarbons.	For use as exterior camouflage finish coat over primed metal surfaces. Combination air-drying and baking may be used. Dried spray dust is extreme fire hazard.
TT-E-529a. Alkyd semi-gloss enamel.	*Class A;* Medium drying-oil phthalic alkyd (typically, linseed-soya modified). No rosin or phenolic resin. *Class B;* Short to medium oil phthalic alkyd plus 10–20% urea- or melamine-formaldehyde resin. No rosin or phenolic or other resin.	IE / IE	BS / BS	A / B	8h / 45m	Good application properties, good resistance to water and hydrocarbon fluids, good flexibility and adhesion, good resistance to weathering.	For use on primed wood and metal surfaces as exterior finish coat, primarily for military and other special equipment. For direct application to bare metal surfaces as interior finish for metal office furniture and lockers, etc. Same uses as Class A enamel, except requires baking.
TT-E-543. Alkyd enamel undercoat.	Long, straight-oil-modified phthalic alkyd resin (air-drying).	I I I I	B	A	7h	Easy brushing, rapid drying, smooth leveling and high opacity.	For use as undercoat for interior gloss and semi-gloss enamels. Plaster, wallboard, and masonry must first be sealed with proper primer-sealer. New wood may be primed with thinned undercoat. Old, glossy, painted surfaces may be coated directly with undercoat before new coat of glossy.
TT-E-545a. Alkyd enamel undercoat, "odorless" (tints and white).	Long, drying-oil phthalic alkyd resin (soya modified).	I I I I	B	A	12h	Easy brushing, rapid drying, smooth leveling, high opacity, good holdout, low odor.	For use as undercoat for interior high gloss and semigloss odorless enamels. Plaster, wallboard, and masonry surfaces must first be sealed with proper primer-sealer. New wood may be primed with thinned undercoat. Old painted surfaces in good condition may be coated directly with undercoat before applying new gloss enamel.

[a] Arranged in sequence by specification letter and number.

[b] Use Code: I—interior; E—exterior; IE—interior or exterior.

[c] Code for Method: B—brush; S—Spray; D—dip; R—roller; BS—brush or spray.
Code for Cure and Drying Time: A—air-dry; B—bake; h—hours; m—minutes. (Note: Baking temperature usually specified is 250 °F [121 °C]).

Note on Drying Time: The figure given is generally the dry-hard or dry-through time specified in the specification and defined in Method 4061 of Federal Test Method Standard No. 141. It may serve as a guide to the time to allow between successive coats, keeping in mind that the actual drying time may vary greatly with the drying conditions (i.e., temperature, relative humidity, ventilation, amount of sunlight, coating thickness, nature of substrate, etc.). Under adverse conditions, a considerably longer drying time than that given in the table may be required. In the case of oil paints and a few other materials, where a dry-hard or dry-through time is not specified or is known to be an inadequate criterion for recoatability, the figure given is a time which experience has indicated as generally satisfactory for recoating purposes. In certain applications, it is desirable to allow a longer drying time for the finish coat to permit it to attain near-maximum properties before placing the coated surface into service.

[d] Where improved hardness and baking properties are desired, these types may be modified by substituting up to 20% of urea- or melamine-formaldehyde resin for an equivalent weight of the alkyd resin. Enamel thus modified shall not be used as an air-drying finish.

Quick-Glance Summary of Important Federal Specifications for Organic Coating Materials (continued)

[a] Specification number and material described	[c] Class or type; nature of resin or vehicle	For use on[b]					Application[c]			Valuable properties	Notes on intended use
		Wood	Metal	Masonry	Plaster	Wallboard	Method	Cure	Drying time		
TT-F-336b. Wood filler paste.	Drying oils and/or varnishes and volatile thinners (free from solvents that adversely affect wood stains of nongrain-raising type), plus high proportion of suitable pigment.	IE					*B	A / B	18h / 1h @ 150 °F (66 °C) *Apply filler with bristle brush. When coat dulls, wipe off excess across the grain, using cheesecloth or other suitable means.		Combination air drying and heat curing type for filling the pores of open grain woods to permit application of a finish with minimum absorption. Apply nongrain-raising stain and shellac-type wash coat, and let dry, before applying filler.
TT-L-26, Cellulose nitrate gloss brushing lacquer.	Cellulose nitrate plus resins and plasticizers, in blend of esters, ketones, alcohols, glycol ethers and hydrocarbons. (Pigmented lacquers must be free of extender pigments).	IE	IE				B	A	4h	Good brushing lacquer, for general use.	For general interior and exterior use as a finish coat over primed metal or sealed wood surfaces. The clear lacquer is suitable for use directly on copper and brass.
TT-L-31. Cellulose nitrate gloss lacquer.	Cellulose nitrate plus medium oil phthalic alkyd resin of nondrying or semi-drying type, with at least 8% of a chemical plasticizer.		E				S	A	6h	High quality lacquer with good resistance to weathering, water and hydrocarbons. Analagous to TT-E-489c alkyd gloss enamel.	For use as an exterior protective coating for metal, particularly smooth clean metal. For refinishing automobiles, trucks, construction equipment, metal signs, railing, etc., or as original finish on such metal items.
TT-L-45b. Multicolor lacquer, aqueous dispersion type (for spray application).	*Type I:* Cellulose nitrate plus non-drying alkyd and rosin-base resin. *Type II:* Like type I, except shall contain no rosin derivatives.	I IE		I IE	I IE	I IE	S S	A A	24h 24h	Good masking of rough, dissimilar, or imperfect surfaces; heavy film can be sprayed in one application; may be applied to damp (not fresh alkaline) surfaces.	For use on interior (Type I) and exterior (Type II) wall surfaces of usual building materials, such as wood, masonry, plaster, wallboard, etc. Also for finishing or refinishing furniture, office fixtures, etc. May be used on suitably primed metal. No primer needed on porous surfaces.
TT-P-0019a. (Army-CE) Acrylic emulsion (latex) paint.	Acrylic polymer dispersed in water, with minimum amounts of necessary additives such as emulsifiers, pigment-dispersants, antifoaming agents, and preservatives.			E			B	A	1h	Easy application and clean-up; freedom from fire and toxicity hazards of organic solvents. Excellent resistance to weathering and yellowing. Quick-drying; may be recoated in an hour.	For exterior use on properly prepared concrete, stucco, and masonry surfaces. No unusual surface preparation required, except cinder block which should be grouted with acrylic fill coat containing white portland cement and washed silica. On previously painted surfaces, remove powdery or flaking material, heavy chalk, and dirt by sandblasting if possible; or, wire-brush surface and seal with penetrating surface conditioner, and let dry before overcoating. White paint is for use

as white only; use special tint base where needed.

Specification	Composition	(1)	(2)	(3)	(4)			Drying	Properties	Uses
TT–P–21. Cement water paint powder (white and tints).	*Type I:* 65% portland cement. *Class A:* Without siliceous aggregate. *Class B:* With siliceous aggregate. *Type II:* 80% portland cement. *Class A:* Without siliceous aggregate. *Class B:* With siliceous aggregate.	---- ---- ---- ---- ---- ----	---- ---- ---- ---- ---- ----	IE IE IE IE IE IE	IE IE IE IE IE IE	B B B B B B	A A A A A A	18h 18h 18h 18h 18h 18h	When properly applied to damp porous concrete or masonry, with fiber brush, dries to hard, opaque, flat, water-repellent, durable coating.	Both Type I and Type II are suitable for interior and exterior concrete and masonry surfaces as decorative, protective, and water-repellent coating. Type II is best for surfaces exposed to excessive moisture, as in swimming pools. For both types, Class A is for general use on all except open-texture masonry; Class B is used for latter.
TT–P–24a. Oil paint, eggshell, ready-mixed (white and tints).	*Type I:* White. *Type II:* Tint-base, white.	---- ----		IE E		B B	A A	18h 18h	When applied on clean dry concrete and masonry, provides eggshell finish having good adhesion, durability, and appearance.	Primarily for exterior concrete and masonry but may also be used inside. Type I is for white only. Type II is for tints. Apply only to dry masonry (cured 3 months to 1 year) free of dirt, form oil, and efflorescence. Do not apply during damp weather or below 50 °F. On open-texture walls, cement-sand grout coat is advantageous. Can be applied over old paint if in sound condition.
TT–P–25a. Primer, oil-base, ready-mixed (undercoat for exterior wood, white and tints).	Mixture of raw and bodied linseed oil with small proportion of pale coumarone resin or ester gum; oleoresinous varnish may be substituted for bodied oil plus resin. (Note: Major portion of pigment is white lead.)	E				B	A	48h	Easy brushing, good adhesion and sealing, good flexibility. Provides good topcoat holdout.	For use on previously unpainted exterior woodwork or on exterior wood previously painted with house paint. Never use as topcoat or leave exposed to weather for long. Normally, should be top-coated within a week or two with a suitable paint (such as that conforming with Federal Specification TT–P–102 or TT–P–103). Toxic (lead); avoid inhalation or ingestion.
TT–P–26a. Fire-retardant paint, interior, (white and tints).	Vehicle not specified, but must meet performance requirements. A suggested vehicle is based on an alkyd resin plus chlorinated paraffin and silicone resin, and containing zinc borate and monoammonium phosphate together with other materials.	I			I	B	A	18h	Required to have good brushing and leveling properties, good resistance to moderate abrasion and to mildew, and low leaching loss, along with fire-retardancy.	For use as a protective and decorative interior fire-retardant paint on wood, plywood, and insulating fiberboard surfaces of interior walls, ceilings, and woodwork; for both new and maintenance painting.
TT–P–28a. Heat-resisting paint (1200 °F).	Vehicle not specified, but must meet specified performance requirements. Manufacturer given wide latitude to produce heat-resisting paint of desired quality.	----	I		I	BS	A	6h	Excellent heat resistance. Capable of useful service for many hours at temperatures up to 1200 °F. Good salt spray resistance.	For use on superheated steam lines, boiler casings, boiler drums, superheated headers, and similar high temperature applications—up to 1200 °F (649 °C).

[a]Specification number and material described	Class or type; nature of resin or vehicle	For use on[b]					Application[c]			Valuable properties	Notes on intended use
		Wood	Metal	Masonry	Plaster	Wallboard	Method	Cure	Drying time		
TT-P-29, Latex-base paint (flat white and tints).	*Type I* (ready-mixed) and *Type II* (paste): Stable dispersion of synthetic resin particles in water (latex); resin must have been prepared by emulsion polymerization and constitute the principal portion of the nonvolatile vehicle.			I / I	I / I	I / I	B / B	A / A	6h / 6h	Easy application, freedom from fire and toxicity hazards of organic solvents, easy clean-up, good washability and scrubbability.	For use both as primer-sealer and finish coat on interior walls and ceilings of wallpaper, plaster, and other porous, absorptive materials. May also be used as finish coat for such materials previously primed with oil-base primer or painted with low gloss wall paint. *Not* suitable for use on bare wood, but satisfactory for wood that has received an oil-base primer. Glossy finishes should be dulled by sanding or washing with solvent type cleaner before repainting.
TT-P-30b, Alkyd flat paint, "odorless" (white and tints).	Vehicle consists of drying oil alkyd resin in odorless-type solvents. Must meet specified performance requirements.			I	I	I	B	A	7h	Easy brushing, good flow and leveling, low odor. Good washability for a flat paint.	For use both as primer-sealer and finish coat on interior walls and ceilings of plaster, wallboard, masonry, and similar materials. Surfaces to be painted must be clean and dry. Masonry usually requires two coats of a special alkali-resistant primer if Portland cement is present.
TT-P-31b, Iron-oxide paint, ready-mixed, (red and brown).	Vehicle of fortified linseed oil type, consisting of mixture of 75% linseed oil, 15% nonreactive spar varnish, and 10% combined drier and thinner (by weight). Thinner to be turpentine and/or mineral spirits.	E	E				B	A	48h	Good brushing properties. Good color retention and good general durability on weathering.	For exterior use as a topcoat on wood and metal. Widely used on tin roofs; often referred to as "roof and barn paint." The small amount of spar varnish and zinc oxide included in the formulation serves to increase the color retention and retard the growth of mildew. Dries overnight to soft film; allow to dry several days between coats. Apply at spreading rate of about 650 square feet per gallon.
TT-P-47a, Oil paint, interior, nonpenetrating-flat, ready-mixed (tints and white).	Treated drying oils or varnish or alkyd resin or a mixture thereof, in turpentine and/or mineral spirits, to yield a product meeting the requirements of this specification. Should be a very long-oil varnish vehicle with a			I	I	I	B	A	18h	Easy brushing, good flow and leveling, good washability for a flat paint, high dry hiding, good sealing properties. Self-priming or self-sealing, "one-coat" type.	For use as a decorative coating on interior walls and ceilings. Can be applied directly to clean dry plaster, concrete, brick, wallboard, wallpaper, and other porous surfaces to give a uniform finish without use of a special primer or sealer. Newly patched areas in plaster should be touched up with the paint and

Specification and title	Composition								Drying time	Characteristics	Uses
TT-P-51d. Oil paint, interior, flat (white and tints).	Vehicle consists of treated drying oils or varnish or a mixture thereof, in a thinner of turpentine and/or mineral spirits. Shall dry to a tough and elastic film. *(minimum oil length of 100 gallons.)*	I	I	—	I			B	A	18h	Easy brushing, good flow and leveling, high dry opacity, good washability for a flat paint.	For use as received on interior walls and ceilings of plaster, wallboard, masonry, and similar materials. A primer-sealer must be used on these surfaces before application of the wall paint. Surfaces must be clean and dry. Masonry usually requires 2 coats of a special alkali-resistant primer, if Portland cement is present. Old painted surfaces in good condition may often be recoated directly with wall paint.
TT-P-53c. Alkyd-linseed oil paint, ready-mixed (medium chrome yellow).	Long oil soya-modified alkyd resin plus some bodied linseed oil, in mineral spirits thinner. (No rosin or rosin derivatives).				E	E		B	A	48h	Good brushing, flow and leveling properties. Good resistance to general weathering.	For outside exposure as topcoat or finish coat on primed wood or metal surfaces. New wood may be primed with undercoater conforming to TT-P-25. Unpainted structural steel may be given prime coat of red lead-linseed oil paint conforming to TT-P-86, or other rust-inhibitive primer. Dries overnight to firm but somewhat soft film; allow 2 or 3 days drying between coats.
TT-P-0055a. (Army-CE) Polyvinyl acetate emulsion (latex) paint, exterior.	*Type I:* Water dispersion of polyvinyl acetate homo-polymer, with dibutyl phthalate and necessary additives.					E		B	A	1h	Easy application and clean-up, and freedom from fire and toxicity hazards of organic solvents. Very good resistance to weathering and to yellowing. Quick-drying—may be recoated in an hour.	For exterior use on properly prepared concrete, stucco, and masonry surfaces. (White paint is for use as white only—not suitable as tint base; use special tint base where desired.) No unusual surface preparation required on new work, except cinder block which should be grouted with polyvinyl acetate fill coat containing white portland cement and washed silica. On previously painted surfaces, remove powdery or flaking material, heavy chalk and dirt by sandblast if possible; or, wire-brush surface, seal with penetrating surface conditioner, and let dry before overcoating.
	Type II: Water dispersion of polyvinyl acetate co-polymerized with a plasticizing monomer, plus necessary additives.					E		B	A	1h		
TT-P-56b. Primer-sealer, oil-type, pigmented (plaster and wallboard).	Any suitable mixture of processed drying oils, or varnish with drier, turpentine, volatile mineral spirits, or a mixture thereof.	I	I	—				B	A	24h	Good brushing and leveling properties. Seals thoroughly in one coat to prevent "suction" spots on subsequent coats. Good flexibility and adhesion.	This primer-sealer is of the "controlled penetration" type, ready to use for sizing interior wall surfaces such as plaster, wallboard, brick, unglazed tile, and concrete. New plaster should dry before priming. Touch up any suction spots with second primer coat before applying finish coats.

(Note for TT-P-51d Uses, continuation at top: "allowed to dry before painting entire area. One-coat coverage sometimes adequate, but usually two coats of paint are required.")

Quick-Glance Summary of Important Federal Specifications for Organic Coating Materials (continued)

[a] Specification number and material described	Class or type; nature of resin or vehicle	For use on [b] Wood	Metal	Masonry	Plaster	Wallboard	Application [c] Method	Cure	Drying time	Valuable properties	Notes on intended use
TT-P-57. Zinc yellow-iron oxide-base primer paint, ready-mixed (for iron and steel).	Type I: 50/50 blend of long oil (linseed) alkyd resin and raw linseed oil.	---	E	---	---	---	BS	A	24h	Easy brushing on rough steel; good penetration and wetting; clings to edges; good weather resistance.	Priming paint for use on bridges and similar rough structural steel, which may be cleaned by only wire brushing, either as shop primer or field primer.
	Type II: Medium oil length (linseed) alkyd resin.	---	E	---	---	---	BS (250°F)	A B	16h 45m	Rapid drying; good durability on exterior exposure.	For use only on smooth, thoroughly cleaned steel as a factory or industrial primer. Primarily for air dry, but may be baked.
	Type III: Straight phenolic spar varnish consisting of 15 gallons tung oil, 10 gallons linseed oil, 100 pounds phenolic resin.	---	E	---	---	---	BS	A	16h	Good resistance to severe humid conditions or fresh water immersion.	For use only on smooth, thoroughly cleaned steel (phosphoric acid pretreatment very valuable), as primer in applications subjected to severe humidity conditions or immersion (e.g., water tanks, dams, equipment in laundries, mines, etc.
										NOTE: All 3 types have good opacity.	
TT-P-59c. Oil-alkyd paint, ready-mixed (international orange).	Blend of 75% raw or refined linseed oil and 25% alkyd resin, plus mineral spirits thinner, and required drier. (No rosin or rosin derivatives.)	E	E	---	---	---	B	A	48h	Vivid color of high visibility. Oil-gloss appearance. Good working properties. Good exterior durability.	For outside use as topcoat or finish coat on properly primed wood and metal. Dries overnight to firm but somewhat soft film, and 2 or 3 days drying should be allowed between coats. Among uses is marking airport roofs. One coat usually adequate on wood shingles. On asphalt shingles, seal with aluminum paint, followed by 2 coats of international orange.
TT-P-61b. Oil paint, black, ready-mixed.	Linseed oil (any mixture of raw, boiled, or bodied oil), plus drier and volatile thinner. (Pigment consists of carbon, lead oxide, siliceous material, and [optional] iron oxide.)	E	E	---	---	---	B	A	48h	Good brushing properties; good hiding; good durability on exterior exposure.	Primarily for exterior use as a topcoat on wood and metal. May be used on exterior wood trim of houses and for painting structural steel surfaces that have suitable priming coats. To make paint dry faster and harder, 1 pint of water-resisting spar varnish may be added to each gallon of paint just before use.
TT-P-71d. Oil-alkyd paint, exterior, chrome-green, ready-mixed.	Long-oil, soya-modified alkyd resin plus bodied linseed oil (75% by weight of alkyd resin solids plus 25% linseed oil).	E	E	---	---	---	B	A	16h	Good flow and leveling properties; dries to smooth film with high initial gloss and good gloss retention. Good	For use as a finish coat on exterior wood and metal trim that has been properly primed. Not suitable for priming or undercoats. Known in the trade as a "trim enamel paint"; for

use on shutters, railings, trellises, and other wood and metal trim. Lead chromate pigment requires precautions against inhalation or ingestion.

Specification	Vehicle / Composition					BS	A	Drying time	Properties (exterior durability)	Uses
TT-P-81c. Oil-alkyd paint, ready-mixed, medium shades, lead-zinc base.	Alkyd resin-fortified linseed oil type consisting of 70% raw or refined linseed oil, 20% long-oil (linseed) alkyd resin, and 10% combined drier and thinner (turpentine and/or mineral spirits).	E	E			BS	A	48h	Brushes easily at spreading rate of 600 to 700 square feet per gallon. Good exterior durability. Variety of medium shades available.	Known as "exterior house paint." For use on properly primed exterior wood and metal. On wood, the priming coat should conform to Federal Specification TT-P-25; on steel, the primer should be of the rust-inhibitive type. For spraying thin with 1 pint of thinner (TT-T-291) per gallon.
TT-P-0085a. (DOD) Reflectorized paint (drop-in type).	Vehicle not specified, but must meet specified performance requirements and test criteria.			E		No-pick-up time	A — 40m		Good resistance to weathering, water, and abrasion; good flexibility; good resistance to bleeding on asphalt or coal-tar; fast drying.	Used to mark airfield runways; glass spheres (beads) provided in separate container. To form reflectorized paint, beads are dropped on surface of applied coating before pigmented binder dries or sets up. Suitable for traffic-bearing surfaces such as concrete, asphalt, brick.
TT-P-0086b. (GSA-FSS) Red-lead-base paint, ready-mixed (for iron and steel surfaces).	Type I: Red lead-linseed oil (blend of raw and pale heat-bodied oil).		E			BS	A	36h	Good wetting of metal despite presence of small amounts of corrosion products impractical to remove. Good weather resistance.	For use as priming or body coats on structural steel and other ferrous metal surfaces where good resistance to corrosive effects of usual atmospheric environments is required. Type I provides better wetting and adhesion; type II gives faster drying.
	Type II: Red lead mixed pigment-alkyd varnish-linseed oil (raw).		E			BS	A	16h	Good weather resistance.	
	Type III: Red lead-alkyd varnish (linseed oil-modified).		E			BS	A	6h	Provides rapid drying, permitting 2 coats in one day.	For use on smooth, thoroughly cleaned steel, as industrial primer or general maintenance primer.
	Type IV: Red lead mixed pigment-phenolic varnish (straight phenolic-tung oil spar varnish of 25-gal. oil length).		E			BS	A	6h	Excellent water impermeability; good resistance to acid and alkaline environments.	For use as a primer on thoroughly clean iron and steel surfaces subject to severe humid conditions or fresh water immersion, such as water tanks, dams, laundries, bottling plants, mines, etc.

NOTES: All four types must be free of rosin or rosin derivatives. Lead pigment requires precautions against ingestion or inhalation, especially when spraying.

| TT-P-0087. (Navy-Aer). Traffic paint, reflectorized (white and yellow). | Either an oleoresinous varnish based on a modified phenolic resin and tung oil, or an oil-modified alkyd resin. | | | E | | No-pick-up time | A — 40m | | Good resistance to weathering, water, and abrasion; good resistance to bleeding on asphalt surfaces; good flexibility; fast drying. | For use on bituminous, brick, or concrete surfaces of streets, highways, and airfields. Type I is for highways; type II for airfields. In each type, class A is supplied with binder and glass spheres separate, class B with binder and glass spheres premixed; type II, class B has extra glass spheres separate, to drop in applied paint. |

Quick-Glance Summary of Important Federal Specifications for Organic Coating Materials (continued)

[a]Specification number and material described	Class or type; nature of resin or vehicle	For use on[b]					Application[c]			Valuable properties	Notes on intended use
		Wood	Metal	Masonry	Plaster	Wallboard	Method	Cure	Drying time		
TT-P-91a. Rubber-base paint (for concrete floors).	Natural or synthetic rubber base with suitable plasticizers dissolved in and thinned with turpentine, volatile mineral spirits, volatile coal-tar solvent (free from benzene), or a mixture thereof.	---	---	I	---	---	BS	A	18h	Good flow and leveling; good resistance to water and detergents, oil and greases, dilute acids and alkalies, and abrasion.	Mainly for *interior* concrete floors subject to dampness, but may also be used on interior masonry walls and steel, where an acid- and alkali-resistant coating is needed. Should not be used over other type paint. Apply only to bare, clean, dry surface (or over same type of paint). Dries mainly by solvent evaporation; provide adequate ventilation. Thin first coat.
TT-P-95. Rubber-base paint (for swimming pools).	Natural rubber base (chlorinated rubber resin), with suitable plasticizers dissolved in and thinned with turpentine, petroleum thinner, coal-tar solvent (free from benzene), or a mixture thereof.	---	---	IE	---	---	BS	A	24h	Good flow and leveling; good resistance to water, detergents, and dilute acids and alkalies; good flexibility.	For interior or exterior concrete or masonry surfaces exposed to water or severe moisture and dampness, such as swimming pools, shower rooms, water plants, filter basins, reservoirs, hydropower plants, and laundries. Not to be used over other type paints; apply to clean, bare, dry concrete. New concrete should age at least two months (tank-like structures should be filled with water) before cleaning, drying, and painting. Three coats recommended. Thin first coat. Use with adequate ventilation.
TT-P-0099a. (Army-CE) Styrene-butadiene exterior emulsion (latex) paint.	Styrene-butadiene copolymer (60% styrene and 40% butadiene) dispersed in water, with minimum amounts of necessary additives such as emulsifiers, pigment-dispersants, anti-foaming agents, and preservatives.	---	---	E	---	---	B	A	1h	Easy application and clean-up; freedom from fire and toxicity hazards of organic solvents. Good weathering resistance. Quick-drying—may be recoated in 1 hour.	For exterior use on properly prepared concrete, stucco, and masonry surfaces. No unusual surface preparation required, except cinder block which sould be grouted with styrene butadiene fill coat containing white portland cement and washed silica. On previously painted surfaces, remove powdery or flaking material, heavy chalk, and dirt by sandblasting if possible; otherwise, wire-brush and seal surface with penetrating surface conditioner (latter must be dry before overcoating). White paint is for use as white only; use special tint base where needed.
TT-P-102. Titanium-lead-zinc and oil	*Class A and Class B:* Mixture of raw or refined lin-	E	E	---	---	---	B	A	48h	Good whiteness or tint retention on outside	For general exterior use on properly primed or previously painted wood

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Specification / Name	Composition				B/BS	A	Drying	Properties	Remarks / Use
paint exterior, ready-mixed (white and light tints).	seed oil (minimum 60% by weight) and bodied linseed oil (16 to 20%), plus drier and thinner to consist of turpentine and/or volatile mineral spirits.							exposure. Good brushing properties. Good resistance to general weathering.	or metal surfaces (particularly wooden structures). Class A paint is for use as white paint only—formulated to chalk freely to maintain whiteness. Class B is formulated for good tint retention—chalks only slightly. On bare wood, prime with TT-P-25 house-paint primer. Metal requires rust-inhibitive primer. No primer needed on previous paint in good condition.
TT-P-103. Titanium-zinc and oil paint, exterior, fume-resistant, ready-mixed, white only.	Mixture of raw or refined linseed oil (minimum 50% by weight) and bodied linseed oil (20 to 26%), plus drier and thinner to consist of volatile mineral spirits and/or turpentine.	E			B	A	8h	Highly resistant to fumes of hydrogen sulfide which would discolor paint containing lead compounds. Good working properties.	For use on properly primed exterior surfaces such as wood and steel where hydrogen sulfide in the air would discolor paints containing lead compounds. Furnished in *white* only. Not recommended for places where fumes do not constitute a problem. On previously unpainted woodwork, three coats should be applied.
TT-P-104. White lead and oil paint, exterior, ready-mixed (white and light tints).	Mixture of raw or refined and heat-bodied linseed oils; types and quantities selected to meet specification requirements. Plus drier and thinner (turpentine and/or mineral spirits).	E			B	A	48h	Very durable exterior house paint. Worn paint leaves surface that needs little preparation. Good adhesion to difficult woods.	This is a pure white lead house paint for general exterior use, particularly on wooden structures; may also be used on metal surfaces. Also recommended for woods that do not hold paint well, such as southern yellow pine and Douglas-fir. Lead pigment requires precautions against ingestion or inhalation.
TT-P-115a. Traffic paint, exterior (white and yellow).	Class A (white) and Class B (yellow): Cooked varnish; may also contain natural and synthetic resins. Manufacturer given wide latitude in choice of materials so long as requirements of specification are met.	E				A	1h	Good resistance to weathering and wear; resistant to light and water; flexible, quick-drying; nonbleeding on bituminous surfaces.	For use on streets and highways subjected to heavy traffic conditions, on both bituminous and cement pavement. May be applied over wide range of temperatures. Not ordinarily for use indoors, but may be so used if adequate ventilation to remove toxic thinner is provided. May be thinned with white gasoline. Prolonged storage may cause settling.
TT-P-00615a. (GSA-FSS) Primer coating, basic lead silico chromate, ready-mixed.	*Type I:* Mainly raw linseed oil, blended with long oil (soya) alkyd resin (4:1 blend).	E			BS	A	36h	Good wetting of metal despite presence of small amounts of corrosion products impractical to remove. Good weather resistance.	For use as priming or body coats on structural steel and other ferrous metal surfaces where good resistance to corrosive effects of usual atmospheric environments is required. Type I provides better wetting and adhesion; type II gives faster drying.
	Type II: Blend of raw linseed oil and medium oil alkyd resin (approx. 1:1 blend).	E			BS	A	16h		
	Type III: Alkyd varnish (linseed oil-modified).	E			BS	A	8h	Provides rapid drying, within an 8-hour period.	For use on smooth, thoroughly cleaned steel, as industrial or general maintainance primer.

Quick-Glance Summary of Important Federal Specifications for Organic Coating Materials (continued)

Specification number and material described[a]	Class or type; nature of resin or vehicle	Wood	Metal	Masonry	Plaster	Wallboard	Method	Cure	Drying time[c]	Valuable properties	Notes on intended use
	Type IV: Straight phenolic-tung oil spar varnish of 25-gallons oil length.	---	E	---	---	---	BS	A	6h	Excellent water impermeability; good resistance to acid and alkaline environments.	For use as a primer on thoroughly clean iron and steel surfaces subject to severe humid conditions or fresh water immersion, such as water tanks, laundries, dams, mines, bottling plants, etc.
NOTE: All 4 types must be free of rosin or rosin derivatives.											
TT–P–636b. Primer coating, synthetic, for wood and ferrous metal.	Medium oil length, oxidizing, phthalic alkyd resin, reducible with mineral spirits; free from rosin, rosin derivatives, and phenolic resin.	E	E	---	---	---	BS BS	A B	18h 45m	Good adhesion, flexibility and durability; hides in one coat.	For priming clean, rust-free, bare or phosphate-treated ferrous metal parts of vehicles, gun mounts, shipping containers, etc. Also as a sealing undercoat on wood parts of vehicles. *Not* intended for immersion or marine use, for severe corrosive environments, or for steel structures that must withstand many years of exposure.
TT–P–641b. Primer paint, zinc dust-zinc oxide (for galvanized surfaces).	Type I: Raw linseed oil (90%) in thinner (10%) of turpentine and/or mineral spirits.	---	E	---	---	---	BS	A	48h	Good adhesion to galvanized metal; high hiding power gives complete hiding in one coat; good resistance to ordinary atmospheric exposure; one coat often adequate on new "galvanize."	For use as priming coat on new or old galvanized metal. Also satisfactory as finish coat except in acidic environments. One coat ample for many service conditions on new galvanized iron. Two coats ample for rusty galvanized surfaces. Chemical pretreatment of metal not required but may be used if desired. Not for use inside water tanks.
	Type II: Long oil, linseed-modified, phthalic alkyd resin in petroleum or terpene thinner. (*May be baked at temperature to 300 °F [149 °C]).	---	E	---	---	---	BS	A B	18h (*)		
	Type III: Straight 100% phenolic resin spar varnish of 25-gallon oil length; oil to be equal parts of tung and linseed.	---	E	---	---	---	BS	A B	18h (*)	Advantages of types I and II, plus good resistance to moisture and water.	For use as above where severe moisture conditions or underwater exposure are met. Chemical pretreatment recommended, using phosphoric acid solutions of the zinc phosphate and phosphate-chromate types.
TT–P–645. Primer paint, zinc chromate, alkyd type.	Long oil soya-modified alkyd resin in petroleum solvent (mineral spirits). No rosin or rosin derivatives to be present.	---	E	---	---	---	BS	A	1h	Corrosion inhibiting even under severe moisture conditions as in marine service. Easily applied.	For use as a corrosion-inhibiting primer on metal surfaces (especially steel and aluminum) particularly in marine service. Suitable as an undercoat for alkyd enamels, as an after pickling primer on steel, and where quick drying is not required.
TT–P–650a. Primer coating, latex base,	Type I: Ready mixed. Type II: Paste. Principal	---	---	---	---	I	BR	A	4h	Easy application and clean-up; freedom	For use on interior walls and ceilings of gypsum wallboard with or with-

Specification and use	Composition					Application	Type	Drying time	Properties	Remarks
interior, white, (for gypsum wallboard).	portion of nonvolatile vehicle of both types to consist of stable dispersion of synthetic latex resin, suitably modified, plus necessary additives.	IE	IE						from fire and toxicity hazards of organic solvents. Does not raise nap of paper layer.	out taped joints. One coat usually sufficient, but two coats may be necessary when finish coat is a solid color. Acid washes not necessary and may be harmful. May be tinted as recommended by manufacturer, but not with colors-in-oil.
TT-P-659a. Primer-surfacer, synthetic, tints and white (for metal and wood surfaces).	Drying oil modified phthalic alkyd resin with necessary amounts of driers and volatile solvents. Free of rosin.	-----	IE	-----		BSD	A B	18h 45m	May be applied by variety of methods. Cures by air drying and/or baking. Good sanding properties. Good adhesion.	For use on wood and metal (hospital) furniture as a primer-surfacer, with a gloss enamel topcoat such as TT-E-491. May be used in a white color as undercoat for white gloss enamels such as TT-E-489. Factory-applied by spray or dip, then baked. For maintenance and re-finishing, apply by brush or spray, and air-dry.
TT-P-662. Primer-surfacer, sanding, lacquer and enamel type.	Cellulose nitrate blended with medium oil phthalic alkyd resin (non-drying or semi-drying type) and maleic anhydride type (or equal) resin.	-----	E	-----		S	A	1h	Very fast drying. Good sanding properties. Can obliterate slight scratches or dents.	For use in both lacquer and enamel refinishing systems, primarily for automotive equipment and other similar metal surfaces. Apply on primed steel prior to application of gloss enamel or lacquer topcoat.
TT-P-664. Primer coating, synthetic, rust-inhibiting, lacquer-resisting.	Resin modified drying oil phthalic alkyd resin (medium oil length), with necessary driers and volatile aromatic solvents to meet requirements of specification. No rosin or rosin derivatives.	-----	E	-----		SD	A	1h	Fast drying; good spraying properties; good adhesion; good weathering and salt spray resistance; rust-inhibiting; lacquer-resisting.	For use as a base coat on bare or chemically treated metal surfaces. Suitable for use under either synthetic enamel or lacquer enamel topcoats. When used for dip process with lacquer systems, the primer may be given a short bake or over-night dry to eliminate possibility of dragging by topcoat.
TT-P-666a. Primer coating, zinc yellow, for aluminum and magnesium surfaces.	Resin modified drying oil phthalic alkyd resin, or blend of alkyd resins, with necessary amounts of driers and volatile aromatic solvents. Rosin acids permitted.	-----	E	-----		SD	A B	1h (*)	Good spraying properties; very fast drying; good weather resistance; corrosion-inhibiting. Lacquer-resistant.	Primarily for use as a corrosion-inhibiting primer on magnesium and aluminum alloy metal surfaces, alone or under enamel or lacquer topcoats. Primarily for spray application. Before applying, metal surface should be chemically cleaned and may be given a pretreatment coating. Apply as semitransparent greenish-yellow coat (0.4 to 0.6 dry film thickness). Avoid full yellow hiding coat.

*(Full hardness in 45 minutes at 250 °F [121 °C]).

TT-R-230. Paint remover (alkali type). Composition not specified, but product must meet all performance requirements of the specification.

For use in stripping alkyd resin, modified urea-formaldehyde alkyd resin, oleoresinous, and nitrocellulose-base finishes from ferrous and nonferrous metals. Items limited to those of size and shape immersible in a boiling solution, unless equipment is available for repeated flushing with hot solution. Stripped surfaces should be thoroughly neutralized by flushing with large quantities of hot water before repainting.

Class 1: For general heavy duty stripping of paint coatings from ferrous metal surfaces (NOTE: Comparison remover is based on sodium hydroxide and trisodium phosphate; can strip a TT-E-485 alkyd enamel in about 35 seconds).

Class 2: For stripping paint coatings from aluminum and other nonferrous metals. (NOTE: Standard comparison remover is based on sodium metasilicate and trisodium phosphate; can strip a TT-E-485 alkyd enamel in about 5 minutes.)

Quick-Glance Summary of Important Federal Specifications for Organic Coating Materials (continued)

[a]Specification number and material described	Class or type; nature of resin or vehicle	For use on[b]					Application[c]			Valuable properties	Notes on intended use
		Wood	Metal	Masonry	Plaster	Wallboard	Method	Cure	Drying time		
TT-R-243. Paint remover (alkali-organic solvent type).	Homogeneous liquid consisting essentially of sodium hydroxide, water, organic solvents, wetting agents, thickeners. No wax, carbon tetrachloride, or benzene. Nonflammable, nonhardening, water-rinsable.		IE	IE			Apply by brush or nonatomized spray; allow time to act as directed in specification. Scrub while flushing with water.				For use primarily for removing multiple coats of paint from steel, especially motor vehicles. May also be used on magnesium, lead, chromium, copper and brass, but unsatisfactory for aluminum, zinc, and tin. Suitable for use on silicate base materials (concrete and other masonry surfaces such as glass, concrete, and brick surfaces should be neutralized with acid before rinsing). Not recommended for wood; unsatisfactory for most plastics. Can be used on rubber if contact time is short.
TT-R-251d. Paint remover (organic solvent type).	Composition not specified, but product must meet all performance requirements of the specification. Shall not stain wood or raise grain; shall not rust or corrode bright steel. Must not contain inorganic alkalies, mineral acids, or carbon tetrachloride. *Type I:* Flammable mixture with paintable retardant. *Type II:* Flammable mixture with nonpaintable retardant. *Type III:* Nonflammable mixture with paintable retardant. Class A: Low viscosity. Class B: High viscosity.	IE	IE								For use in removing paint (in scrape-off operations) from wood and metal surfaces. All three types should be capable of removing air-dried single coat films of oleoresinous and alkyd coatings, but may not be effective with all the newer synthetic-base coatings; however, type III is most satisfactory for baked-on air-dried multiple coat systems. Types I and III do not require solvent cleaning prior to repainting; type II does. The more viscous removers are recommended where surfaces are largely vertical. Paint removers are toxic; use with care and adequate ventilation.
TT-S-176b. Surface sealer, varnish type (for wood or cork floors).	Phenolic-tung oil varnish of 25-gallon oil length; resin to be para-phenyl phenolformaldehyde. *Class 1:* Minimum nonvolatile content 40%; for floors and flooring having rapid and high absorption. *Class 2:* Minimum nonvolatile content 25%; for floor and flooring of relatively dense structure.	I					B	A	7h	Good sealing properties; seals by absorption, without leaving a surface film.	For sealing and treating new or old wood or cork floors and floor coverings. Open-grained wood or cork tile should be treated with wood filler before sealing.
TT-S-190. Sanding sealer, lacquer type	Nitrocellulose lacquer with minimum nonvolatile	I					S	A	1h	Dry to sand in one hour. Good sanding proper-	This is a lacquer type sanding sealer for use on wood furniture. It may

Specification	Composition	Use					Grade	Grade	Drying time	Properties	Remarks
(for wood furniture).	content of 18%, and zinc stearate as sanding agent as about 5% of the nonvolatiles.									ties.	be used in conjunction with stain, washcoat, and filler—as sanding coat before application of lacquer finish coats.
TT-S-300. Shellac, cut (supersedes TT-V-91b, shellac varnish).	Solution of dry lac resin (free from rosin or copals) in 95% alcohol, specially denatured. *Type I:* Bleached (white). *Type II:* Orange. Both types furnished in 2 grades: Grade A—regular. Grade B—refined. and in 3 bodies: Body 1 (light = 4-pound cut. Body 2 (medium) = 4½-pound cut. Body 3 (heavy) = 5-pound cut. Body 4 (very light) = 3-pound cut.	I	(*)				B	A	1h	Easily applied; pleasant odor; quick drying; excellent sealing properties; durable, mar-resistant (but discolors when wet with water, and is attacked by alcohols); does not darken with age; easily retouched.	For use as a sealer and finish coat for interior wood floors and wood furniture. Thin before use and apply in thin coats to achieve maximum properties. White shellac must be fresh (preferably not over six months old) to ensure complete drying without after-tack. Grade A is suitable for most purposes; grade B is used where freedom from wax and maximum clarity are needed.

*Shellac varnish may be used on hardboard and pressed wood surfaces as sealer or finish coat. Also used as a knot sealer for wood.

Specification	Composition	Use					Grade	Grade	Drying time	Properties	Remarks
TT-S-706. Oil stain, opaque, for exterior wood.	Linseed oil and driers in a volatile thinner composed of turpentine, mineral spirits, V.M. & P. naphtha, kerosine, or a mixture of these. (Pigments must be opaque inorganic types free from lakes or toners).	E					BD	A	24h	For use primarily as an opaque, durable stain for exterior wood, but may also be used on new or unfinished interior wood that has been sanded and dusted. Stain is particularly suited for smooth planed wood; on sawed surfaces or rough wood, thinning is desirable. Available in red, brown, or green. Best applied at time of construction, by dipping cut pieces into stain or brushing on all sides to cover wood completely. Keep stain thoroughly mixed to avoid streaking. (Interior stains covered by TT-S-711.)	
TT-S-00708. (AGR-FS) Oil stain, semi-transparent, for exterior wood.	Boiled linseed oil with small proportions of raw or bodied linseed oil, paraffin wax, and pentachlorophenol—in a volatile thinner containing at least 85% mineral spirits.	E					B	A	48h	Durable stain for exterior wood; permits grain and texture of wood surface to show through to a fair extent; usually lasts 3 years or more.	For use on either smooth or rough exterior wood surfaces where protection against wood weathering and dimensional changes afforded by multiple coats of oil paints is not necessary; useful for house siding, fencing, signboards and the like, but not for frames, windows, or doors. Paraffin wax prevents overcoating. Cannot be applied over old paint or varnish. Apply only one coat to avoid glossy patches.
TT-S-711a. Oil stain for interior wood.	With some latitude to manufacturer in selection of raw materials, to consist of suitable earth colors ground with drying oil and reduced to specified consistency with suitable thinner. Shall be miscible with mineral spirits conforming to TT-T-291, grade I.	I					B	A	48h	Dries and penetrates slowly so brush marks and excess can be wiped off; does not raise grain or obscure it.	For general use on interior wood surfaces. Apply with brush, let soak for half-hour, and wipe off all excess. For lighter color, wipe off sooner. Will cover 400 to 500 square feet per gallon. May be thinned with volatile mineral spirits or turpentine, if desired. Let dry thoroughly before finish coats.

Quick-Glance Summary of Important Federal Specifications for Organic Coating Materials (continued)

[a]Specification number and material described	Class or type; nature of resin or vehicle	For use on[b]					Application[c]			Valuable properties	Notes on intended use
		Wood	Metal	Masonry	Plaster	Wallboard	Method	Cure	Drying time		
TT-T-51c. Asphalt varnish.	Hard native asphalts or asphaltites, fluxed and blended with properly treated drying oils and thinned with suitable solvents, plus driers. (This specification is met by a 7-gallon, heat-bodied linseed oil-Gilsonite varnish).	---	IE				B	A	24h	Good resistance to water. Yields smooth, black, lustrous finish. Low cost.	This is a general utility asphalt varnish for both indoor or outside exposure. Particularly suited for painting indoor water and gas pipes. Exterior durability is limited unless sheltered from sun.
TT-V-71d. Oleoresinous varnish, interior, floor and trim.	Composition not specified beyond indicating this to be an oleoresinous varnish of 45% minimum nonvolatile content, but must meet all performance requirements of the specification.	I	---	---	---	---	B	A	7h	Rapid drying; good gloss; water-resistant.	For general use on interior wood, particularly floor and trim. *Not* for use where rubbing properties are a prerequisite; a rubbing varnish is covered by Fed. Spec. TT-V-86.
TT-V-81b. Mixing varnish for aluminum paint.	Composition not specified, but product must meet requirements of the specification.	---	---	---	---	---					This varnish is for mixing with aluminum powder or paste *on the job* to make an aluminum paint. *Class A* varnish has a lower viscosity than Class B, and is for use with aluminum powder. *Class B* is for mixing with aluminum paste.
	Type I: 120% Kauri reduction (very long oil varnish).	E					BS	A	24h		For use as a vehicle for aluminum paint for the painting of exterior wood. A 75- or 80-gallon linseed ester gum varnish will meet this specification.
	Type II: 75% Kauri reduction (medium oil varnish).		IE	IE	IE		BS	A	18h		For making a general purpose paint for use on such surfaces as metal, properly cured concrete, plaster, and the like, both indoors and outside. Phenolic resin varnishes of 25- to 30-gallon oil length will meet this specification. They have better water resistance than type I varnish.
TT-V-109. Spar varnish, alkyd-base.	Vegetable-oil-modified phthalic alkyd resin, with necessary thinners, driers, and anti-skinning agents. Free from rosin or rosin derivatives.	IE	---				BS	A	18h	Yields clear smooth film with good adhesion and flexibility on wood.	Primarily for use as a transparent protective finish for wood. Also suitable for use as an aluminum vehicle.
TT-V-119. Spar varnish, phenolic resin-base.	100-percent oil-soluble phenolic-resin varnish of 33-gallon oil length. Largely tung oil-modified, with small amounts of castor	E	E				BS	A	8h	Dries rapidly to smooth lustrous finish; excellent exterior durability and water resistance; good adhesion	For use as a marine spar varnish and as a varnish for structural and architectural use on exterior wood. May be mixed with aluminum powder or paste to give protective finish coat

| | oil and alkali-refined linseed oil, in thinner plus driers. | | | | | | | and flexibility. | for wood, metal, and doped fabrics, and as a sealing compound in the fabrication and repair of riveted aluminum alloy tanks. On bare wood, apply 3 coats. |
| TT-V-00121d. (COM-NBS) Spar varnish, water-resisting. | Clear air-drying oleoresinous varnish, containing not less than 55% non-volatile matter by weight. Exact nature of vehicle not specified, but must meet all performance requirements of the specification. | IE | IE | ------- | B | A | 8h | Rapid drying; excellent durability on exterior exposure and indoors; excellent water resistance. | For use as a general utility, water-resisting spar varnish for exterior and interior exposure, where durability is the chief requisite, and where high initial hardness of the film is not required. |

FIGURE 8.3. *Cinder-block test house for evaluating durability of coatings for masonry surfaces.*
Wall specimens for paint exposure tests are shown in foreground.

FIGURE 8.4. *A typical masonry-wall specimen used to conduct paint exposure tests.*

9. Selected Bibliography

The following is a selected bibliography of important reference works, specifications, and articles found useful in preparing this monograph or considered to be valuable sources of further information in the field of organic coatings. While not in itself an exhaustive list, it provides basic references which, in many instances, are good sources of further references to the more detailed literature.

The Bibliography is divided into two main sections. The first is a list to which specific reference has been made in the text. These specific references indicate immediate sources of further information about the material or topic under discussion. Included are references to a number of Military ("MIL") specifications of particular usefulness. Federal ("TT") specifications for organic coatings, while referenced to some extent in this bibli-

ography, are covered more comprehensively in the tabular summary of Federal specifications presented in Chapter 8. Since Government specifications are in a continuous state of change which precludes up-to-date subletter listings except in current indexes [67, 68], reference in the Bibliography is to the basic specification only, with the understanding that the latest revision in effect is the one normally applicable.

The second section of the Bibliography lists works of general usefulness in the field of organic coatings, including some volumes dealing with the theoretical aspects of polymer chemistry and the properties of organic coating materials. These general references are arranged alphabetically by author (except where the title is of over-riding significance) and are not numbered.

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