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Chapter 4
Coating Types and Characteristics

4-1. Introduction

a. All coatings—whether used for corrosion protection, to provide good aesthetics or a pleasing appearance, or for any other purpose—will contain a film-forming material. This material may be organic or inorganic and, after application, may form a hard, impervious film, a soft porous film, or combinations in between. Furthermore, the film-forming material may be clear (unpigmented) or filled with a variety of different pigments, depending on its function. When the film-forming material (resin) contains pigments, it is called a binder. The binder will hold the pigment particles together and to the substrate over which it has been applied. When the binder (resin plus pigment) is dissolved in a solvent to make it liquid, the combination (solvent, binder, and pigment) is considered to be a vehicle. The term vehicle comes from the ability to transport and apply the liquid to the surface being coated. Once on the surface, the solvent evaporates and the vehicle becomes a pigment-binder system. Application properties of the paint usually are characterized by the vehicle in a liquid condition. The viscosity, rate of solvent evaporation, and consistency of the wet coating are most important during application. After application, the pigments determine the corrosion-inhibitive properties and, generally, the color and some flow control properties of the applied coating. The binder determines the weatherability of the coating, its environmental resistance, and the coating's ability to function in a given environment. The required surface preparation, and often the application equipment and techniques, are determined by the binder.

b. The principal mechanisms by which binders form films are reaction with oxygen from the air (oxidation), evaporation of the solvent from the vehicle (solvent evaporation), or chemical crosslinking (polymerization). The coating film attained by these mechanisms can be either thermoplastic or thermosetting. Thermoplastic materials deform and soften on exposure to heat. Thermoset materials do not deform and remain hard upon heat exposure. Each type of coating resin or binder categorized by its film-forming mechanism, different types of pigments, and the various solvent families will be discussed. Drying oils are an integral part of some coating formulations, and they as well as driers that aid in the drying reaction will be covered. Miscellaneous additives that are formulated into many coatings for specific purposes are itemized and discussed. Sections are presented on powder coatings, thermal spray organic and inorganic coatings, and galvanizing tapes and wraps. Problems with VOCs also will be discussed.

4-2. Film-Forming Mechanisms

Coating binders can be subcategorized according to the mechanism described above. However, with both oxidation and most polymerization film-forming mechanisms, solvent evaporation occurs initially, followed by a subsequent chemical reaction consisting of either a reaction with oxygen or chemical crosslinking. Solvent evaporative coatings also are called thermoplastics because, when heated, they become plastic and can soften and deform. Oxidation and chemically crosslinked coatings "set" and harden when cured; they do not soften or deform on heating and, therefore, are called thermosets. After application, most coatings "dry" by solvent evaporation to form a film that feels dry to the touch. However, the dried coating may not be cured, and additional chemical reactions may be required. Oxidation coatings require crosslinking with oxygen from the air, and polymerization coatings require a crosslinking chemical reaction between two or more coreactants to attain their final physical and chemical properties.

a. Oxidation (thermoset). Thermoset coating types dry and ultimately crosslink by reaction with oxygen from the atmosphere. All such coatings in this class contain drying oils that consist mainly of polyunsaturated fatty acids. The drying oil frequently is combined with a resin, usually by cooking or heating to enhance water and chemical resistance. The curing reaction is accelerated by the presence of metallic salts as driers. After application, the coating dries by solvent evaporation. However, to attain maximum chemical and moisture-resistance properties, the oil must react with oxygen from the air to crosslink, cure, and further harden. The auto-oxidation reaction occurs at a relatively fast rate shortly after application of the wet paint; and it continues throughout the life of the coating, although at a much slower rate. For most oil-based coatings, suitable moisture and chemical resistance occur within a few days after application, although maximum resistances may not be obtained until months or years after application. In time (often 20 or 30 years later), the oxidation reaction and continued drying of the oleoresinous binder system leads to cracking, embrittlement, and deterioration of the coating film.

b. Solvent evaporation (thermoplastic). A second film-forming mechanism is solvent evaporation. The solvent within which the resin is dissolved or emulsified may be water or an organic solvent. The liquid resin returns to a solid material when the solvent evaporates. The coating is formed as a result of solvent evaporation and drying, with no attendant crosslinking or polymerization. Solvent-based coating systems that dry solely by solvent evaporation (vinyls and chlorinated rubbers) have their usage severely restricted because of VOC regulations. These resins must be dissolved in relatively high amounts of noncompliant solvents to be formulated into a corrosion-resistance protective coating. Latex emulsion coatings consist of pigmented synthetic resin particles emulsified in water. Because latex emulsion coatings dry by water evaporation (and perhaps one percent or less of a coalescing organic solvent), coatings formulated in this fashion comply with VOC legislation; and they have rapidly advanced in recent years to become environmentally safe, long-lasting, protective coating systems. Thermoplastic coatings in the context used here are coatings that dry principally, or solely, by water or solvent evaporation; they do not undergo chemical crosslinking. Principal coatings in this class are acrylic lattices, solvent cutbacks, and hot melt bituminous coatings and vinyl coatings (zinc chromate vinyl butyral wash primers, vinyl chloride-vinyl acetate copolymers, and waterborne vinyls).

c. Chemically crosslinked (thermoset). Thermoset coatings, by definition, are coatings that are “set,” and are nondeformable when exposed to elevated temperatures. Thermoset coatings achieve their characteristic “set” and the ability to resist heat deformation by virtue of a three-dimensional crosslinking. This crosslinking is achieved by coreacting two or more monomers, with at least one monomer having a functionality of three or greater, and the other a functionality of at least two. (The functionality is the number of reaction sites where crosslinking can occur.) This film-forming mechanism involves a chemical reaction combining smaller molecules (mers) to create a larger molecule (polymers). The reactions can consist of the same kind of mer units reacting to form larger molecules (homopolymers) or different mer units reacting to form copolymers, tripolymers, or, generically, polymers. After crosslinking, and depending on the type and extent of crosslinking, the resin system is solvent resistant, ranges from tough and flexible to hard and brittle, and does not significantly deform on the application of heat. In coating formulations, most coreactive coating systems are supplied in multipack systems consisting of two or more containers that must be mixed prior to application. However, some thermoset materials react with moisture from the air (moisture and ketimine curing isocyanates) and can be supplied as a one-package system. After application in all instances, the coating system, when properly applied and cured, forms a single, extremely large molecule by virtue of its polyfunctional crosslinking. When suitably dissolved in a solvent and pigmented, many coreactive materials can be formulated into a protective coating. Some of the more commonly used protective coating systems are based on catalyzed epoxy resins, polyurethane reactions, acrylic/vinyl ester resins, and modifications thereof. Each of these coating systems will be discussed later. Polymerization reactions are becoming increasingly important in the formulation of modern VOC-compliant coating systems. Small molecule units, that by virtue of their low molecular weight are liquid, can be reacted with other low molecular weight liquid molecules to form a higher molecular weight molecule that will harden to form a solid (nonliquid) protective film. The most successful adaptations to manufacturing low VOC coatings have been two-pack, chemically cured coating systems such as the epoxy, polyurethane, polyester, and vinyl ester systems.

4-3. Binders (Resins)

The binder, sometimes called a resin, and a suitable solvent (to make it liquid) are combined to form the vehicle. Pigment particles then are dispersed and mixed into the liquid resin, and the paint is packaged, usually in a can or pail, for sale. Upon use, the liquid paint is applied—perhaps by brush, roller, or spray—after which the solvent volatilizes, the liquid resin dries or cures, and the pigment particles “bind” together and to the surface being painted. Binders may be natural or synthetic resins and may be organic or inorganic. The binder used in a particular coating system is primarily responsible for the coating's chemical, water, and UV light-resistant properties. However, to optimize protective capabilities, most coatings must be pigmented to provide color and opacity, to reduce shrinkage, and to obtain enhanced moisture and chemical resistance. When properly applied and dried and/or cured, the pigmented binder provides the decorative, protective layer referred to as a paint or coating. The characteristic of the binder and its method of drying and/or curing determines the mechanism of film formation. Many of the natural resins used as binders are derived from exudations from trees or insect secretions. Synthetic binders are generally by-products of chemical refining or manufacturing processes. These resins are man-made and, when refined and modified for coatings use, can be used as film formers for protective and decorative coatings. Because of their improved moisture, chemical, and UV resistant properties compared with the natural resins, synthetic resins have obtained widespread use in a variety of different service environments as corrosion-protective coatings.

a. Natural resins (oxidative). Natural resins are derived from tree exudations, fossilized vegetable remains, or insect secretions. Natural resins derived from tree exudation may be named after the region from which they originated; this accounts for some exotic names such as Kauri, Batu, Sandric, and others. Natural resins generally are cooked with drying oils to make varnishes with faster drying rates, higher gloss, and harder films than can be attained from the oil alone. Some were used as a sole binder in so-called spirit varnishes, i.e., the resin was simply dissolved in volatile solvents. When applied to a surface, the solvent evaporated from the spirit varnish leaving a film of the resin on the substrate. This type of drying mechanism involves no substantial chemical change and is typical of what today is called lacquer. In general, clear films of natural resin, oil varnishes, and spar varnishes have poor exterior durability. Accordingly, these resins are no longer used extensively except for interior use such as for wood furniture finishing.

(1) Rosins. The natural resin, rosin, is obtained from oleoresin, a sap exudation of pine trees. Lighter fractions (i.e., the fastest evaporating, when heated, also usually the lowest molecular weight) of the sap include turpentine, dipentene, and pine oil. Rosins generally have a high acid value and poor resistance to water and alkalies. They also are sensitive to oxygen in the air and are tacky to the touch. Rosins are most commonly used to produce rosin maleic esters, and they are adducted (partially reacted) with maleic anhydride and then esterified with glycerol. These esters sometimes are combined with castor and/or soya oils to reduce yellowing and to increase the hardness and gloss of paints. Coatings manufactured from rosin maleic ester binders are clear and unpigmented and are intended for interior wood surfaces and furniture finishes.

(2) Shellac. Lac is a resinous secretion of a coccid insect from India and Thailand used to make shellac. The dry secretion is collected, crushed, and washed. Afterward, it is melted and dried in sheets that are broken up and exported for use as an alcohol-soluble coating resin. The shellac film is both hard and fairly elastic, and it has a variety of uses including knot sealers and sealers for wood and plaster.

(3) Copals. Natural resins called copals are derived from fossilized or semifossilized vegetable remains. These resins have high carboxyl-functional hydrocarbons of high acid number and, therefore, are reactive. The fossil resins frequently are cooked with vegetable oils to result in a resin with an improved drying time, hardness, gloss, and water or alkali resistance. Because of their flexibility, these resins most commonly are used for coating paper (paper labels).

b. Oil-based alkyds (oxidative).

(1) Alkyd resins are derived as a reaction product of polyhydric alcohols and polybasic acids. Alkyds use a polybasic acid derived from a semidrying or drying oil so the resin formed can undergo auto-oxidation at any temperature. This definition also includes polyester resins, of which alkyds are a specific type. The properties of alkyd coatings predominantly are the result of the properties of the drying oil used in the manufacture of the alkyd resin. Drying time, hardness, color, and moisture sensitivity all depend on the drying oil, its type, and the degree of unsaturation (available crosslinking sites). Soybean oil has been shown to give good drying rates and good color retention. However, linseed oils generally dry faster but darken on exposure to light. Castor and coconut oils have good color-retentive properties and are used as plasticizing resins because of their nonoxidizing characteristics.

(2) The amount of oil combined with the resin influences the protective capability of the applied alkyd coating. Long oil modifications (greater than 94.6 liters [25 gallons] of oil per 45.36 kilograms [100 pounds] of resin) result in less moisture and chemical resistance and longer drying times. However, long oil alkyds have a greater ability to penetrate and seal a poorly cleaned surface. Short oil alkyds (less than 37.85 liters [10 gallons] of oil per 45.36 kilograms [100 pounds] of resin) are fast-drying coatings that usually require baking to attain full cure (approximately 95 °C (200 °F)) for a few minutes. Short oil coatings have good moisture and chemical resistance but are relatively hard and brittle. Medium oil alkyds (37.85 to 94.6 liters [10 to 25 gallons] of oil per 45.36 kilograms [100 pounds] of resin) are a practical compromise between the long and short oil modifications. They usually dry hard within 24 hours and are the oil length of choice for most new and maintenance alkyd coating systems.

(3) All alkyd coating systems initially dry by solvent evaporation and cure by auto-oxidative crosslinking of the oil constituent. Because of the presence of the drying oil, alkyd coating systems have limited chemical and moisture resistance, cannot be used in highly chemical environments (acid or alkali), and are not resistant to immersion or near immersion condensing conditions. However, their relatively low cost, ease of mixing and application, and excellent ability to penetrate and adhere to relatively poorly prepared, rough, dirty, or chalked surfaces make them the coating system of choice on steel exposed to nonchemical atmospheric service. Alkyd coatings are widely used for structural steel such as the exterior of buildings, handrails, cranes, gantries, etc. Alkyd coating systems should not be used in immersion or in environments in which the coating will be subjected to prolonged wetting, dampness, or condensing humidity. Because drying oils are saponified by alkalies, they should not be applied to alkaline surfaces, including applications over galvanizing (as a result of the alkaline nature of zinc hydroxide, a corrosion product of zinc), concrete, mortar, and most cementitious surfaces (as a result of inherent alkalinity because of the use of lime as a component of cement).

c. Alkyd modification (oxidative). Alkyds are perhaps the most widely used industrial protective coating by virtue of their ease of application, relatively low cost, color stability, and good weather ability in most atmospheric environments; therefore, it is reasonable to assume that coating formulators would seek to improve properties of the drying oil alkyd by modification with other resin types. Although these modifications will somewhat increase the cost of the coating system, improved properties usually result and make the modification cost effective.

(1) Phenolic modification. Modification with a phenolic resin improves gloss retention, water, and alkali resistance. Phenolic alkyd resins have performed satisfactorily in water immersion, a service in which nonphenolic modified alkyd resins are not suitable.

(2) Vinyl modifications. Alkyd resins with vinyl modification are commonly formulated as universal primers. These primers generally can be topcoated with most generic-type intermediate and topcoats. The alkyd constituent improves adhesion, film build, and solvent and thermal resistance; the vinyl modification enhances recoatability and chemical and moisture resistance. These coatings frequently are used as shop primers or as tie coats between different generic coatings (e.g., over inorganic, zinc-rich primers or between alkyd primers and epoxy topcoats).

(3) Silicone modifications. Silicone modification of alkyd resins is perhaps the most widely promoted modification for corrosion-protective coatings. A silicone intermediate is added to the alkyd resin in quantities up to 30 percent to provide polymers with greatly improved durability, gloss retention, and heat resistance. Moisture resistance is greatly improved by the silicone modification, and this type of paint is used extensively as marine and maintenance paint.

(4) Epoxy modifications. Alkyd resins can be combined with epoxy resins to produce coatings with improved chemical and moisture-resistant properties. Epoxy ester coatings are similar to alkyds, and they are used when improved performance is required. Epoxy esters result from the direct esterification of an epoxy resin and a fatty acid such as a vegetable oil or rosin. The resulting epoxy ester resin is prepared by reacting it with drying oil by heating in the presence of an esterification catalyst. The same drying oils used to prepare alkyds also are used to prepare epoxy esters. Oil length is categorized as long, medium, and short with properties similar to those for alkyds. Epoxy resin oil-based coatings have better adhesion, moisture, and chemical resistance than alkyds, although they are slightly more expensive. These coatings are used as baking and air dry original equipment manufacturers' coatings applied to appliances, machinery, pumps, valves, etc.

(5) Urethane modifications. Alkyd resins are commonly reacted with isocyanates to form a so-called uralkyd or urethane oil coating. The isocyanate reaction decreases the drying time of the coating and provides enhanced resistance to chemicals, moisture, weathering, and abrasion. Uralkyd coatings are used as marine coatings of wood boat hulls, machinery enamels, and an upgrade to an alkyd coating.

d. Waterborne acrylic emulsion coating. An emulsion is essentially a dispersion of droplets of one liquid in another liquid, in which the first is not normally soluble. Examples of emulsions are milk and mayonnaise; in both of these, fat globules are disbursed in water. For paints, emulsion technology is promising for VOC compliance because water is not a restricted solvent, and only small amounts of solvents—called coalescing solvents—are required in the formulation. The resin is polymerized to a relatively high molecular weight (10,000 or higher) in emulsion paints. The pigment is incorporated in the resin, and the semisolid resin-pigment polymer is emulsified in water. Acrylic polymers are especially popular as an emulsion resin because they provide coatings with unexcelled color retention and have excellent exterior weathering and durability properties. The hardness and flexibility of emulsion polymers vary considerably because of the types and amounts of monomers used in their molecular weights. Methyl methacrylate monomer gives the hardest thermoplastic polymer, and acrylate monomers yield the softest product. Copolymers of acrylic and methacrylic esters are used extensively for exterior acrylic emulsion paints. Vinyl acetate-acrylic copolymers also are popular, particularly for interior use. The acrylic constituent upgrades water and alkali resistance, film flexibility, and durability; and it acts as a permanent plasticizer for the vinyl acetate.

(1) Styrene-acrylic. Styrene-acrylic waterborne systems in which the styrene is copolymerized with lower alkylacrylates have gained in importance. They are characterized by high gloss and good gloss retention. When properly formulated, they dry quickly and develop good film hardness. Styrene-acrylic systems are used primarily as interior house paints or as coatings for relatively mild interior industrial service conditions. These coatings may yellow on exterior exposure and do not have good moisture resistance. They also are used as concrete block fillers.

(2) Latex emulsions. Latex emulsion coating systems have gained in popularity because of their ease of application and cleanup and their good color retention and durability on exterior surfaces. One hundred percent acrylic copolymer formulations have been developed that provide good protection as complete water-based systems (primer, intermediate, and topcoat) on blast-cleaned structural steel. Acrylic latex coating systems also are used extensively for protecting aluminum and other nonferrous metals and for

painting wood in exterior weathering environments. Because they are also VOC compliant, acrylic latex coating systems have gained popularity as shop-applied systems. Even more popular are latex emulsion intermediate and/or finish coats used in conjunction with a water-based, inorganic, zinc-rich primer. Water-based, zinc-rich primers, coated with acrylic emulsion intermediate and top coats, are rapidly becoming popular because of their VOC compliance, good corrosion protection, and aesthetic properties. Although many of the acrylic emulsion coating formulations have dramatically improved moisture resistance, these coatings are not recommended for use in areas of high condensing humidity, ponding water, splash zones, or for immersion service. The ionic surfactants used in the emulsion to provide in-can stability will result in water sensitivity after application. Water vapor transmission may be a problem for wood or masonry surfaces, and latex paints may be suitable for these surfaces because they are said to breath. Breathing occurs as a result of irregularities during the coalescence part of film formation. A series of pores or defects in the coalesced film allow passage of water vapor but retain the larger liquid water molecule. Water-based paints develop poor film properties when applied in cold, damp weather. Both cold weather and high humidity or dampness retard water evaporation and the drying and coalescence of the paint film. The result can be a soft, poorly adherent film that, when drying finally occurs, may be cracked or brittle with poor adhesion. Too fast a water evaporation rate on a hot surface can lead to a powdery, poorly adherent paint or a film with many voids, pinholes, or cross-sectional porosities. Storing emulsion paints at excessively high temperatures for prolonged periods or freezing the emulsion may destabilize it and cause settling, de-emulsification, and/or severe viscosity changes.

e. Bituminous (solvent evaporation). Bitumens used in the coatings industry are coal tar and asphalt. These materials are distinctly different physically and chemically; but in appearance they are essentially identical black, thermoplastic, tar materials. Coal tar enamels, or pitches, are derived from the coking of coal. When coal is heated in the absence of air to a temperature of approximately 1093 °C (2000 °F), it decomposes partially into a gas and a coke. Coal tar is formed when the gas is subsequently condensed. Lighter oil fractions are removed from the tar by subsequent heating and gas extraction until the desired coal tar composition for use in coatings is obtained. Asphalt may be mined or obtained as a residue from the distillation of crude petroleum. Lighter fractions are removed during distillation until the desired asphalt tar suitable for coating use is obtained. Asphaltic coatings have much greater UV resistance than the coal tars, and they are suitable for use in above-grade atmospheric weathering applications. However, coal tar coatings are vastly superior to asphaltic coatings in moisture and chemical resistance. Because of UV light-induced cracking, unmodified coal tar coatings most commonly are used below grade or in water-immersion service. Thermoplastic bituminous coatings are applied as hot melts, solvent cutbacks, or water emulsions.

(1) Hot melt. Hot melt application involves heating the bitumen to a temperature of approximately 178 °C (350 °F) to 246 °C (475 °F); its viscosity at that temperature is low, almost waterlike. The hot melt then is applied by mop or swab to the surface being coated, although other techniques such as brush, rolling, or spraying may be used. Flow coating of the interiors of pipes and small vessels also is possible. In this method, the hot melt is flowed onto the pipe or vessel while the item is rotated or turned. In general, hot melt applications provide the best moisture and chemical resistance, followed in order by solvent cutback and water emulsions. Pipelines coated with hot melt coal tar have 100-year successful exposure experience underground and in water immersions. In the pipe coating shop, the pipe is blast-cleaned to SSPC-SP 10 metal by a rotary blast machine. The bitumen is flow-coated onto the pipe with alternate reinforcement of asphalt- or coal tar-impregnated felt paper. The finish wrap is of kraft paper for UV protection. Field application of a hot bitumen is best done by swabbing with a mop. However, swabbing is rarely done at present because of safety considerations and the development of suitable, safer, alternate coatings that are more easily field applied.

(2) Solvent cutback. Asphaltic or coal tar bitumens are dissolved in a suitable solvent (aliphatic and aromatic hydrocarbon solvents). Dissolving the bitumen in a solvent lowers its viscosity enough that the cutback can be applied by brush, roller, or spray as appropriate. After application, the solvent volatilizes and the bitumen resolidifies into a film. The coating thickness and moisture resistance of a solvent cutback is considerably less than that achieved by hot melt application, but the convenience of not having to heat the bitumen at the jobsite immediately prior to application is a major advantage. Cutbacks are used on pipelines, pump stations, below grade, and immersion applications when hot melt bitumens cannot be applied.

(3) Water emulsion. Water emulsions are prepared by suspending minute particles of the bitumen in water using emulsifying agents. Pigmentation with inert fillers such as coal dust, powdered silica, mica, and limestone dust may be incorporated with the bitumen. After application, the water evaporates and coalescence occurs to form a protective film. Latex emulsions (both asphaltic and coal tars) are widely used as driveway or parking lot sealers and as waterproofing agents. Bitumen latex emulsions are VOC compliant. Some solvent cutback applications may not be VOC compliant

because of the use of solvents; and hot applied, hot melt bitumens may release VOCs into the atmosphere during heating and application. Furthermore, volatile phenol-containing compounds produced during the heating of the bitumen are considered carcinogenic and skin irritants. Accordingly, suitable worker protection must be provided in the form of protective clothing and appropriate respirators.

f. Vinyl (solvent evaporating copolymer). Most vinyl coatings consist of a resin comprised of a copolymer of PVC and polyvinyl acetate (PVA) in the ratio of approximately 86 percent PVC to 13 or 14 percent PVA. Approximately 1 percent or less maleic acid is used as a modifier to provide adhesion to metallic surfaces, and the same amount of hydroxyl modification (using a vinyl alcohol) provides adhesion to vinyl butyral wash primers or other organic coatings. Increasing hydroxyl modification of vinyl chloride or vinyl acetate resins enables the incorporation of the vinyl into alkyds, epoxies, and other resin systems. This incorporation improves air dry, moisture resistance, and compatibility. Maleic acid modification to the vinyl chloride-vinyl acetate copolymer improves adhesion to blast-cleaned steel, zinc-rich coatings, or other metal surfaces. Additionally, the carboxyl groups introduced into the vinyl copolymer resins provide points of reactivity for crosslinking reactions.

(1) Vinyl chloride. Vinyl acetate copolymer coatings have been used extensively by USACE for protection of submerged steel or as a coating systems specified for the protection of steel used in locks and dams. Because of the high amounts of solvents that must be used to dissolve vinyl resins, most vinyl coatings, except water-based vinyl formulations, are not VOC compliant.

(2) Vinyl butyral wash primer. Basic zinc chromate vinyl butyral wash primers have been used extensively as primers to provide excellent adhesion to a variety of surfaces, including carbon steel, stainless steel, zinc, cadmium, tin, aluminum, galvanized steel, magnesium, and even glass. These wash primers are preferred when exposure to salt water or salt spray occurs because they inhibit underfilm corrosion. Basic zinc chromate and vinyl butyral wash primers formulated in accordance with DOD-P-15328 D incorporating a vinyl butyral resin, basic zinc chromate pigments, and a phosphoric acid alcohol solvent system have been used extensively in the past. For best performance, wash primers should be topcoated with a coating based on a hydroxyl modified vinyl solution resin. This is an especially effective system in seawater and freshwater immersion and in corrosive environments. Wash primers have many application particularities. If an all-vinyl system is desired, the wash primer must be coated with a hydroxyl modified vinyl solution coating. The maleic acid modified vinyl resin coatings in common use in USACE will not adhere to the wash primer. Many other coatings adhere well to the wash primer, including oil-based alkyds, epoxies, and urethanes. When mixing, the acid diluent must be added slowly to the base with agitation to prevent local gelation. These wash primers should be used within 8 hours after mixing; any primer remaining after 8 hours should be discarded because there will be a gradual decline in adhesion of the mixed wash primer. There may be no physical change in appearance after 8 hours but adhesion will be diminished substantially. The mixed wash primers must be applied thin (as a “wash”) to a thickness not exceeding approximately 1.9 cm (3/4 mil). Coating failures may result if mixing and application instructions are not followed. Vinyl wash primers range in VOC content from 680 to 765 grams/liter (g/L) (5.7 to 6.4 lb/gal). (To convert grams per liter to pounds per gallon, divide by 119.8, for example, 250 g/L ÷ 119.8 = 2.1 lb/gal).

(3) Vinyl chloride-vinyl acetate copolymers. These vinyl solution coatings are noted for outstanding toughness and water resistance. USACE has used a five-coat vinyl system for years on steel exposed in both freshwater immersion and atmospheric service on locks and dam gates. Although the five-coat system is somewhat expensive to apply, it is extremely durable when properly applied. Repainting intervals of more than 20 years are commonplace, although maintenance repainting and touchup of deteriorated or damaged paint may be necessary at more frequent intervals. The common USACE vinyl system uses a vinyl resin containing 86 percent polyvinyl chloride, approximately 13 percent polyvinyl acetate, and maleic acid modification. The coating system has excellent toughness, moisture resistance, and light resistance; and it can be topcoated easily after extended periods of time. Generally, PVC-PVA copolymer coatings range in VOC content from 540 to 650 g/L (4.5 to 5.4 lb /gal).

(4) Waterborne vinyl. Vinyl resins and modified vinyls frequently are emulsified vinyls modified with acrylic resins to provide enhanced flexibility, toughness, and recoatability. Vinyl acrylics are most commonly used for exterior surfaces. Waterborne vinyl coatings consisting of pigmented polyvinyl acetate are formulated for interior use. The polyvinyl acetate can be used alone as a homopolymer, or it can be coreacted with other monomers such as the lower molecular weight esters of acrylic, fumaric, or maleic acid. Latices based on polyvinyl acetate generally have relatively poor moisture resistance, light fastness, and exterior durability. They are not the preferred choice for exterior surfaces, although they are eminently suitable for interior use. Polyvinyl acetate based homopolymer and copolymers are relatively inexpensive, and they are easy to apply and clean up. These emulsion coatings are suitable for

interior use and exterior nonaggressive environments. However, an acrylic modification is required when greater moisture and exterior weathering resistance is needed.

g. Catalyzed epoxies (crosslinking copolymers). The epoxy resin most commonly used for industrial protective coatings is of the glycidal-ether type, specifically, that derived from bisphenol-A and epichlorhydrin. This combination of raw materials yields a series of related compounds that, prior to crosslinking, have an epoxide group at each end of the molecule, and a alcoholic hydroxyl group as a midchain pendant. Crosslinking takes place preferentially through the terminal epoxy groups then through the midchain hydroxyl groups. Other epoxy resins have been developed, including cycloaliphatic epoxies, that offer improvements in light stability and UV light degradation; but these epoxy resins do not exhibit the adhesion, chemical resistance, and flexibility of resins derived from epichlorhydrin and bisphenol-A. Epoxy cresol novolacs also have been developed and provide high temperature resistance and great chemical resistance at the expense of brittleness and a lack of toughness and flexibility. The epoxy molecules, particularly those of the bisphenol-A type, are relatively small and must be coreacted with copolymer curing agents to attain crosslinking properties sufficient to provide a protective coating. The copolymer crosslinker frequently is called a catalyst or curing agent, and it usually is a polyamine- or polyamide-containing material.

(1) Polyamine curing agents for epoxies. The polyamines (i.e., diethylenetriamine, hydroxyethyldiethylenetriamine, bishydroxydiethylenetriamine) are relatively small molecules with a low molecular weight compared to the epoxy resin. When reacted, they lead to tight crosslinking and high chemical and moisture resistance. However, during the crosslinking reaction, any unreacted amine may be squeezed out of the crosslinked film to the surface and develop the so-called amine blush, a hazy white coloration on the coating surface. The blush, a reaction between the amine and carbon dioxide from the air, is not detrimental and can be allowed to remain on the surface unless topcoating is necessary. However, the blush must be removed by wiping or washing it from the surface (it is water soluble) before a subsequent epoxy coat is applied. To minimize formation of the amine blush, many formulators require a 15- to 30-minute induction time after mixing prior to application. This allows the reaction to begin and initial crosslinking to occur before the paint is applied. Some of the small amine molecules will partially crosslink with the epoxy resin molecules and increase their size and reduce the tendency for migration.

(a) Polyamine crosslinked epoxy coatings generally have excellent alkali resistance and the greatest chemical resistance of the epoxies. They also have good moisture and water resistance. These epoxies are the most brittle and the least flexible; and they have a strong tendency to degrade on UV light exposure, resulting in chalking. Amine-cured epoxies, with suitable nonreactive pigments, are used widely as tank lining systems for the protection of steel and concrete in water and aqueous chemical immersion service. Because of their high crosslink density (achieved as a result of the small molecular size of most of the amines used as coreactants), amine-cured epoxies are the epoxies of choice in atmospheric or immersion environments of high and low (pH 3-12+) hydrolyzing chemicals.

(b) Phenolic modification to the epoxy resin further enhances water resistance; and phenolic modified epoxies, with amine coreactants, are perhaps the most popular coating system for freshwater and saltwater immersion and many aqueous chemical solutions, even at elevated temperatures. Phenolic modification enhances moisture and heat resistance properties of the epoxy, but it imparts slightly more brittleness and diminishes alkali resistance.

(c) Polyamine crosslinked epoxy coatings are readily formulated as VOC-compliant coating systems as a result of the low molecular weights of both the amine and epoxy coreactants. If a relatively low molecular weight bisphenol-A epoxy is used, both the epoxy and amine coreactants are in liquid form. Little if any solvent is needed to dissolve or dilute the resins, and 100 percent solids coatings are feasible.

(d) Amine adduct epoxies were developed to reduce the tendency toward amine blushing; to eliminate an induction time; and to make the low molecular weight amine less volatile, safer, and easier to mix. An amine adduct is prepared by reacting an excess of a polyfunctional (three or more reactive sites) amine with some of the epoxy resin to increase its molecular size. The prereacted amine adduct then is packaged in a separate container, sometimes with additional pigment and solvent. As with all other coreactant curing agents, the components in the separate containers are mixed prior to application. Because of the greater molecular size of the amine adduct relative to the unprereacted amine, amine blush is eliminated and most of the other problems associated with small molecular weight amines are minimized. Chemical crosslinking in the applied film is not considered to be as extensive as that provided by the nonprereacted amine, and the chemical resistance is somewhat less. However, application is much easier and not nearly as dependent on thorough mixing and adequate induction time.

(2) Polyamide curing agents for epoxies. Polyamide curing agents are the condensation products of a dimerized fatty acid with the polyamine. Terminal amine functionality allows crosslinking to occur as with a straight amine, although the polyamide molecule is much larger. The crosslinked film has improved flexibility, improved gloss and flow, excellent water resistance, and good chemical resistance. However, polyamide-cured coatings have somewhat less solvent and alkali resistance than amine- and amine-adduct-cured epoxies. Because fatty acids have a water repellent tendency, polyamide-cured epoxies are said to be tough, flexible, water-repellent coatings. Compared to the amine and amine-adduct types, polyamide-cured epoxies have significantly better UV light resistance, resulting in substantially less chalking on exterior exposure. Polyamide-cured epoxies are perhaps the most widely used of the three types of curative systems, and they have wide application in the protection of steel and concrete in freshwater and saltwater immersion. Polyamide-cured epoxies have the best exterior weathering resistance and the best ability of the epoxies to recoat after extended periods. Polyamide epoxies are used to protect substrates exposed to condensation and high humidity. Specially formulated polyamide-cured epoxies have the ability to displace water from a surface. These coating materials can be applied and cured under water to form corrosion-resistant coatings.

(3) 100 percent solids epoxies.

(a) The 100 percent solids epoxies can be formulated from low molecular weight polyfunctional liquid epoxy resins. The viscosity of these resins can be lowered even further by the use of compatible reactive diluents with an epoxy functionality of one; they do not contribute to crosslinking but are chemically bound into the final crosslinked film. The liquid epoxy resin system is crosslinked by a liquid polyamine or polyamide without the addition of any solvent. A tertiary amino phenolic catalyst, such as tri-(dimethylaminomethyl) phenol may be added to produce polymerization of the epoxy resin with itself. This and other phenols act as accelerators in the curing reaction. Silicone resins may be added as flow agents, and dibutyl phthalate can be added as a plasticizer. Thus, the entire liquid paint can be converted to a crosslinked coating that becomes a 100 percent solids epoxy. These materials have little, if any, volatile organic material so they are VOC compliant. Coatings formulated in this fashion show typical epoxy finish properties; but they are less flexible than other epoxies because the films are thicker and the close spacing of the reacting groups leads to a high crosslinked density. The film is tough and relatively nonbrittle. Solventless epoxy systems have low internal stress and are less brittle because there is negligible volume contraction on curing to a solid.

(b) The 100 percent solids epoxies generally have short pot lives because the coreactants are not diluted. Some formulations require the use of special twin-feed airless spray equipment for external mixing (refer to paragraph 8-2*g*). When aromatic polyamines are used for curing, hardening times of 4 to 12 hours can be attained even at temperatures as low as freezing. Although these coating systems are relatively expensive, they are used primarily as corrosion-resistant linings for storage tanks (e.g., oil tankers), both on land and in marine vessels. Because of their low molecular weight liquid formulation, these materials also can be used as self-leveling epoxy flooring systems. These coating systems generally are clear or high gloss and, when applied, have a waterlike consistency that hardens to a smooth, glossy flooring.

(4) Coal tar epoxies.

(a) Coal tar epoxy is a combination of a coal tar and an epoxy resin. The epoxy resin usually is packaged separately from the curing agent, which frequently is combined with the coal tar resin. The curing agent may be an amine, amine addict, or polyamide. The crosslinking reaction is the same as those previously described, with active hydrogens from the amine nitrogen providing a crosslinking site to the epoxide groups and, in some situations, the hydroxyl groups of the epoxy resin. The coal tar acts as a filler within the crosslinked epoxy matrix, and the resulting film has the toughness, adhesion, UV resistance, and thermal stability of the epoxies combined with the extremely high moisture resistance afforded by the coal tar. The amine-cured coal tar epoxies generally have great chemical and moisture resistance but are more brittle and harder to apply and topcoat than the amine adduct and polyamide-cured coal tar epoxies. The polyamide-cured coal tar epoxies are more water resistant, flexible, easier to topcoat, and more tolerant of application variables than the other epoxies.

(b) One problem with coal tar epoxies is recoating. The recoat window for application of a coal tar epoxy topcoat to a coal tar epoxy undercoat can be as little as 18 hours with some formulations, and with most formulations it usually is within 48 hours. Extensive intracoat disbonding may occur after this time. The disbonding is believed to result from low molecular weight hydrocarbon oils from the coal tar exuding to the surface after application and from UV light-induced oxidation. Amine-cured coal tar epoxies are more susceptible to this phenomenon than the amine adduct and polyamide types. However, even with the latter types, the first coat may cure so hard and glossy after only a few hours that adhesion of subsequent coats may be a problem. To attain adhesion between an undercoat and subsequent coats of a coal tar epoxy, it may be necessary to roughen the surface by sweep blast cleaning or other scarifying techniques and to remove the oxidation and exudate products. Alternately, slow evaporating strong solvents such as methylene chloride and diacetone alcohol can be applied to the coal tar surface being overcoated. These solvents will penetrate, attack, and partially dissolve or swell the coal tar epoxy surface so molecular entanglement and adhesion may occur. However, because these solvents are slow evaporating, they may be retained within the coal tar epoxy film. If the coal tar epoxy is immersed in water, these relatively polar solvents may attract water and blistering may occur. Therefore, care should be taken when using solvents to increase intracoat adhesion for coal tar epoxies in immersion service. The problem is of much lesser consequence if the coal tar epoxy is used on an atmospheric or nonwater immersion surface.

h. Urethanes (crosslinking copolymer). Crosslinking reactions in urethane coatings consist of a reaction between an isocyanate containing (-N=C=O) material and a material with a polyhydroxylated (-OH) containing coreactant. Crosslinking occurs because of the high reactivity and affinity of the isocyanate group for the active hydrogen of the polyolhydroxyl or any other active hydrogen atom attached to a nitrogen or oxygen atom. The rate of this crosslinking reaction depends on a number factors, such as the type and configuration of both the isocyanate and polyol materials and temperature. However, the reaction is such that, with most formulations, crosslinking can occur at temperatures as low as 18 °C (0 °F) or less.

(1) Isocyanates. The isocyanate reactant can be either aromatic (containing the benzene ring) or aliphatic (straight chain or cyclical) hydrocarbons. Aromatic polyurethanes are prone to darkening and yellowing on exposure to sunlight because of the chromophoric nature of the benzene ring. Because aliphatic polyurethanes, by definition, do not contain the benzene ring, they do not yellow or darken and are preferred for exterior use.

(a) The most important monomeric diisocyanates used for coatings are toluene diisocyanate (TDI), 4,4, diphenylmethane diisocyanate (MDI), and 1,6, hexamethylene diisocyanate (HDI). Because of their irritant characteristics, these materials rarely are used in unreacted form for the compounding of urethane coatings. They normally are converted into isocyanate terminated polymers or adducts of polyols such as hydroxyl terminated polyesters and polyethers. The molecular weight of these isocyanates can be increased by self-reaction in the presence of catalysts to form dimers and/or trimers.

(b) Aliphatic isocyanates react more slowly and are considerably more expensive than the aromatic isocyanates, but they allow the formulation of nonyellowing, light stable, high gloss finish coats. The appearance of polyurethane coatings formulated with aliphatic isocyanates are unsurpassed in this regard by any of the epoxies, acrylics, or other coating materials. One of the most important aliphatic isocyanates is HDI. In its monomeric form, HDI is an irritant as is true with TDI and MDI. However, HDI can be reacted (commonly with water) to obtain a higher molecular-weight modification that is less volatile and safer. When HDI or its higher molecular-weight modifications are reacted with a suitable polyol in the presence of certain metal catalysts (tin, bismith, zinc, iron, cobalt), a urethane coating with excellent resistance to discoloration, hydrolysis, and heat degradation is produced.

(c) Because of the potential presence of unreacted monomeric forms of TDI, MDI, and HDI—all of which are respiratory irritants—an air-fed respirator should be used when mixing and applying these materials. Workers and painters may never develop an isocyanate sensitivity, or the sensitivity may occur only after prolonged exposure. However, some individuals may become sensitized quickly, on initial contact or on only a short exposure. When isocyanate respiratory sensitization occurs, it occurs suddenly and drastically, and the affected individual should be removed from the work site. The sensitization is permanent, and increased exposure leads to increased irritation to affected tissues and membranes (refer to Chapter 10).

(2) Polyols. Polyols coreact with isocyanates to form a polyurethane film. A polyol consists of large molecules (commonly acrylics, polyesters, polyethers, epoxies, vinyls, and alkyds) that have been reacted with di- or polyfunctional alcohols such as propylene glycol, trimethylolpropane, pentaerythritol, and others. The hydroxyl-terminated polyol materials are packaged separately from the isocyanate, and the packaging usually includes appropriate solvents and pigments. On application, the isocyanate and polyol constituents are mixed and crosslinking proceeds via the isocyanate-hydroxyl functions and liberates a carbon dioxide gas. To prevent bubbles and voids in the coating cross-section as a result of the carbon dioxide gas inclusion, all polyurethane coatings must be applied relatively thin (0.038 to 0.05 mm [1.5 to 2.0 mils] per coat). This allows the gas to pass easily from the coating before the coating cures and hardens. In general, the characteristics and properties of the urethane coating depend predominantly on the properties of the polyhydroxylated coreactant. The VOC content of most polyurethane coatings ranges from 250 to 550 g/L (2.1 to 4.6 lb/gal).

(3) Acrylic urethanes. Acrylic urethanes are perhaps the most widely used urethanes for corrosion protection and

atmospheric service. When properly formulated, these materials have excellent weatherability, gloss, and color retention and good chemical and moisture resistance. They can be tinted easily and pigmented to provide a variety of deep and pastel colors at a lower cost per gallon than the next most popular class, the polyester urethanes. Acrylic urethanes are not used for water immersion service and, for the most part, they do not have the chemical resistance of the polyester urethanes. However, they have excellent weathering and color retentive properties when an aliphatic isocyanate coreactant is used. These are the most popular aliphatic polyurethanes; they are widely used as topcoats over epoxy primers and intermediate coats in most nonchemical atmospheric environments. Many water tanks, bridges, railroad cars, aircraft, and other highly visible structures are coated with these light-fast, glossy, aesthetically appealing coatings.

(4) Polyester urethanes. As a result of their high isocyanate demand when coreacted, polyester urethanes form relatively hard, chemical-resistant poly films. Because they are tightly crosslinked, they have great chemical and moisture resistance; but they are not as flexible and tough as the acrylic urethanes. This high isocyanate demand also substantially increases the cost of polyester urethane over acrylic urethanes. Polyester polyurethanes are used in exterior chemical environments in which acid fumes or highly corrosive conditions are encountered. They have high gloss, are light fast, and have a good appearance.

(5) Polyether urethanes. The polyether prepolymer is considerably less expensive than either acrylic or polyester polyols. However, polyethers are sensitive to UV-induced oxidative degradation. Ether linkages within the polyether are somewhat water sensitive; and, in polyethers, they are repeated throughout the polymer chain without separation by long water-insensitive hydrocarbon chains or aromatic groups. Polyester polyurethanes are used as elastomeric urethane coatings, for coal tar urethanes, and for other urethane coatings that are sheltered or protected from light. They frequently are used as pipeline coatings or for below grade corrosion protection, and coatings for minimum service.

(6) Epoxy polyurethane. Epoxy urethanes are considerably more expensive than conventionally cured amine or polyamide crosslinked epoxies. The epoxy addition induces a tendency for an epoxy urethane to chalk, and the lower moisture resistance resulting from the urethane crosslink produces a less chemical- and moisture-resistant polymer than a conventionally cured epoxy coating. Most epoxy urethanes are formulated with a less expensive aromatic isocyanate. They are promoted primarily as low-temperature-curing epoxies; as fast curing, chemically resistant urethanes for interior use; or as primers in exterior exposures.

(7) Vinyl polyurethanes. Urethane coatings using vinyl polyols combine abrasion resistance of the urethane with the toughness, flexibility, and chemical resistance of the vinyl. These urethane coatings are promoted for use when flexibility and abrasion resistance are important. However, vinyl urethane coatings are subject to some chalking or fading on exterior exposure and do not have the color, gloss, weatherability, or solvent resistance of the acrylic and polyester urethanes. Because the vinyl is thermoplastic and is attacked and softened by solvents, recoating after extended periods is not a major problem and is a primary advantage of vinyl urethane systems. Coatings based on these resins are used on structural steel, ships, tanks, and other steel structures for which corrosion resistance flexibility and abrasion resistance are important.

(8) Moisture-cured polyurethanes. Isocyanates can react with the hydroxyl group in water (H-OH) to form a unique class of coatings known as moisture-cured urethanes. Single package moisture-cured urethanes use an isocyanate prepolymer that, when applied, reacts with the humidity in the air to form a tough, hard resinous film. Because of their rapid rate of reaction, aromatic isocyanates are used almost exclusively in moisture-cured urethanes. The pigments must be essentially nonreactive with the isocyanate. Although it is possible to use a number of pigments, aluminum leaf is common. Properly formulated and applied, urethanes have excellent adhesion to blast-cleaned structural steel surfaces. When spray applied, urethanes form a tough, glossy, highly protective chemical and solvent-resistance film. Because of their high crosslink density, the recoat window of some formulations is less than 24 hours, or it may be more than a month in exterior environments. Sufficient solvent hardness and permeability does not occur in 24 hours, and topcoating is considered safe. Topcoating is also safe after a month or more of exterior chalking and weathering to remove the slick, glossy surface that often occurs shortly after curing. However, within the range of 24 hours to a month or more, subsequently applied polyurethane topcoats may exhibit disbonding or poor adhesion. Moisture-cured urethanes are used as primers under some epoxies, used as full system coating on steel and nonferrous metals, and as primers on marginally cleaned steel. Frequently, the moisture-cured polyurethane primer and/or intermediate coats are topcoated with a nonmoisture-cured aliphatic polyurethane to minimize yellowing and darkening.

i. Vinyl ester (crosslinking copolymer).

(1) Strictly speaking, vinyl esters can be called vinyls because of the vinyl unsaturation ($-C=CH_2$) on the epoxy

backbone chain; actually, they are manufactured from and are closely related to acrylics. Methacrylic esters of bisphenol-A or other epoxies, such as novalacs, are prepared by reacting methacrylic acid with terminal oxirane groups of the epoxy. The resins have high viscosity at room temperature and are mixed with monomeric styrene, which acts as a reactive diluent to reduce viscosity. Crosslink curing is by free radical initiation generated from peroxide degeneration using benzyl peroxide, methyl ethyl ketone peroxide, or peroxide blends.

(2) Compared to normal unsaturated polyester resins, vinyl ester resins have better chemical resistance because of the stability of the epoxy backbone and the presence of stable methyl groups on the methacrylate terminations. Compared to a polyester resin, there are fewer points of unsaturation on the backbone, and even these are effectively shielded by methacrylate terminations. Vinyl esters have excellent resistance to acids and alkalies, bleaches, and other oxidizing agents. Vinyl esters are used as thick film (1.02 to 1.52 mm [40 to 60 mils]) tank and chimney linings when great strength and high chemical resistance are required. They most commonly are applied by spray, have a short potlife, and build readily to thicknesses approaching 0.50 mm (20 mils) per coat. Because of their short potlife and high chemical and solvent resistance, topcoating after even a short period of time (as little as 3 or 4 days) may be a problem with some formulations. Because the coatings are applied so thick and because of high inherent shrinkage stresses on curing, a deep anchor pattern (0.10 to 0.13 mm [4 to 5 mils]) is required for most applications. Care must be taken to ensure that the coating is not applied excessively thick, or cracking may occur.

(3) Vinyl ester coatings can be applied as highly pigmented, sprayable coatings or with a fiberglass veil reinforcement as fiberglass reinforced plastic laminants. Vinyl ester coatings have excellent abrasion and wear resistance, and these attributes combined with their chemical resistance lead to application as high build monolithic concrete floor systems and tank linings. Because of their high volume solids content and because styrene is used as a reactive diluent (combined thinner and coreactant), little thinner is required in a formulation. Thus, vinyl ester coatings are VOC compliant.

4-4. Drying Oils

a. If a drying oil is reduced or dissolved in a solvent and pigmented, a drying oil coating results. Not all oils are drying oils. An oil is classified as drying if, when spread out in the air as a thin layer, it changes from a liquid to a solid film with a great strength, toughness, and hardness. This drying ability depends on the molecular structure of the various chemical compounds that make up the oil. Specifically, the oil must have polyunsaturated fatty acids, commonly ethylenic carbon double bonds (-C=C-). When combined with oxygen and accelerated by metallic driers, auto-oxidative polymerization occurs and transforms the oil from a liquid to a solid. Some vegetable oils (e.g., cottonseed, rapeseed, peanut, and coconut oils) are not drying oils. Fatty vegetable oils that exhibit proper drying oil characteristics and can be formulated into paints or protective coatings include linseed, tung, soybean, dehydrated castor, oiticica, and fish oils. Linseed oil, one of the most widely used drying oils, is obtained from pressing the flax seed. Raw linseed oils dry too slowly for most purposes; therefore, they require processing and the addition of driers to hasten the hardening rate.

b. Processing usually consists of heating the raw oil and dissolving mixtures of manganese and cobalt driers—which are soluble in the oil at ordinary room temperatures—in the raw oil. The oil can be further treated by bodying, which consists of blowing gasses (oxygen and/or hydrogen) through the oils to increase viscosity and reduce drying time. All of these treatments (heating, blowing, and adding driers) result in an increased oil viscosity that occurs as a result of auto-oxidative crosslinking polymerization and oxygen absorption into the oil film. In general, bodied oils (those that have been thickened by heat treating and blowing air through them) dry more quickly, are tougher, and have better water, chemical, and after-yellowing resistance than untreated, unbodied oil. However, bodied oils do not wet and penetrate as well. Even if blown or bodied, drying oils may have their properties enhanced considerably by the addition of a synthetic resin. When added to the processed and treated drying oil, synthetic resins (e.g., alkyds, phenolics, epoxy esters, or urethanes) enhance the chemical and moisture-resistant properties of the drying oil.

c. Animal oils, principally menhaden fish oil, have properties similar to drying vegetable oils, except they are somewhat slow drying, become tacky in humid weather, and give off an unpleasant odor in confined spaces. Animal oils are not recommended for interior use, and they frequently are combined with other drying oils.

d. In a strict sense, oil paints consist of a pigment, a drying oil, and an aliphatic solvent used to thin the pigmented oil. The oil is not modified with any synthetic resins. The coating initially dries by solvent evaporation; this is followed by auto-oxidative crosslinking of the drying oil. The addition of driers to the oil aid in the formation of the solid film. The characteristics of these oleoresinous paints are determined primarily by the characteristics of the drying oil, and to a lesser degree by the pigments incorporated into that oil. Because these paints have a high oil content, drying times are slow with 2- to 3-day recoat periods over the soft film. However, long oil paints were formulated for use over poorly prepared, rusted, and/or mill scale surfaces; so for these situations, long oil paints may be the best paints.

4-5. Driers

Driers are materials that promote or accelerate the curing or hardening of drying oil paints. Drying of oil-based paints by auto-oxidation is affected considerably by temperature and the presence of certain catalysts. Driers act as a catalyst to aid in both surface and through drying of drying oil paints. Driers are considered metallo-organic materials that can be classified as surface driers and through driers. The metal constituent is lead, cobalt, zinc, or manganese; the organic radical of the metallo-organic dryer is usually a naphthenate derived from naphthenic acid. Surface driers are compounds of cobalt and manganese. The use of these materials will cause a surface of the drying oil paint to rapidly set to a near solid, but the underlying paint does not reach this advanced state of oxidation. In thick films an uneven hardening will cause wrinkling; therefore, through driers should be used in conjunction with surface driers. Through driers are metallo-organic compounds of lead, cadmium, zinc, or zirconium. When used in conjunction with surface driers, through driers help cause auto-oxidative crosslinking through the cross-section of the film. Driers may lose their effectiveness with prolonged storage. This storage problem affects the primary surface driers (cobalt and manganese) and, to a lesser degree, secondary driers (calcium and zinc). The loss of dryer effectiveness is believed to result from the absorption and deactivation by certain pigments, notably carbon black. If an oil-based paint is aged, it may be best to test its ability to dry by applying some of it to a nonabsorptive surface to see if it dries properly.

4-6. Pigments

Virtually, all protective coatings used for corrosion protection contain pigments. Although the obvious purpose of pigmentation in a coating is to provide color and opacity, proper formulation of pigments into a protective coating does far more than that. For corrosion-protective coatings, pigments function by providing inhibition or passivation of a metal surface, preventing corrosion; reinforce the paint film; act as a barrier to provide water impermeability to the dried paint film; and with zinc-rich coatings, sacrifice galvanically to protect the underlying steel substrate (refer to Chapter 2). Certain pigment types enhance heat, abrasion, acid, or alkali resistance to coatings. Pigment particle size and shape, ease of wettability by the binder, and bulking or properties relating to specific density contribute significantly to the viscosity and application characteristics of the wet coating and, ultimately, properties of the dried, protective coating.

a. Inhibitive pigments. A select few pigments provide active corrosion inhibition to metal substrates when formulated into a coating composition. These pigments are slightly water soluble; and, when the paint film is exposed to and permeated by moisture, the water in the film cross-section partially dissolves constituents of the pigment and carries it to the underlying metal surface. The dissolved ion species react with the metal (commonly steel or aluminum) to form a reaction product that passivates the substrate and reduces the rate of underfilm corrosion.

(1) Chromate. Chromate-containing pigments (e.g., zinc and lead chromates) partially solubilize, liberating the chromate anion that, when carried by moisture to the underlying steel or aluminum substrate, reacts to form a chromate film on the metal surface. This chromate film strongly passivates the metal surface and prevents establishment of electrochemical corrosion cells by reducing electron transfer. Additionally, this passivating film is slightly alkaline, which further inhibits underfilm corrosion. To a lesser degree, molybdate and borate pigments also provide active underfilm passivation, but not nearly as well as the chromate-containing pigments.

(2) Lead and zinc. Lead and zinc also may disassociate partially on moisture permeation into a paint; these elements also provide inhibitive protection, but in a different fashion. When pigmented into oil-based coatings, lead and zinc react with acidic degradation products that occur as a result of oxidation and UV light exposure. If these complex organic acids reach the underlying steel, under-film corrosion may be hastened. However, the lead and zinc cations react with the acids complexing, insolubilizing, and/or neutralizing them. Lead and chromate pigments are considered hazardous paint ingredients, and many coating formulators are restricting or eliminating these materials from their formulations. Although substitute pigments may be safer, they may not offer the inhibitive properties of the pigments they replace.

b. Barrier pigments. Barrier protection is offered to a greater or lesser degree by all inorganic pigments formulated into a coating. Any permeating moisture must migrate around the pigment particle and, by so doing, increase its permeation path length to the substrate. However, some pigment types are specifically formulated as barrier pigments, or alternately impart barrier properties to the paint film. Most notable of the barrier pigments is flaked aluminum.

(1) Aluminum flake. Aluminum flake, in the form of a leafing aluminum (coated with a stearic or other fatty acid to cause it to be displaced to the surface by the coating binder) or nonleafing flake (noncoated), is specifically added to many types of coatings, particularly oil-based coatings and epoxy mastic coatings to enhance UV light resistance and reduce moisture permeation. No other pigments can provide the leafing properties that aluminum flake does. Leafing aluminum pigments are widely used in alkyd finish coats to provide a bright, shiny appearance and for resistance to atmospheric weathering (UV) and moisture.

(2) Micaceous iron oxide. Micaceous iron oxide, commonly used in Europe and to a lesser degree in the United States, has lamellar (platelike) particles. Any relatively large sized pigment particle, even if it is not plate shaped, will increase the permeating path of moisture and result in a barrier-type protection. Some recently manufactured pigments consist of hollow glass spheres that have been developed to aid in VOC compliance and to fill a coating and make it more moisture impermeable.

c. Sacrificial pigments. High purity zinc dust, with little zinc oxide or carbonate contamination, is the only sacrificial pigment used in paint manufacture. These zinc dust pigments consist of particles that are of a relatively large (1 to 3 µ) diameter and are essentially pure zinc. If the zinc pigment particles are in contact with both each other and the underlying steel surface when incorporated with a binder into a dry paint film, galvanic protection results. On the galvanic series zinc is anodic to steel and becomes the anode in a zinc-steel galvanic couple. The zinc anode corrodes and dissipates, and the underlying steel cathode remains galvanically protected. This phenomenon occurs for all zinc coatings, including those deposited by hot dip galvanizing and thermal spraying. Thermally sprayed aluminum coatings (both aluminum powder and wire) also are believed to have sacrificial capability when applied to blast-cleaned steel. However, this sacrificial capability may last for only a short time—within a few days after application until the aluminum oxidizes sufficiently to insulate the aluminum from the steel. Galvanic protection ceases after a sufficient thickness of intact aluminum oxide forms on the sprayed aluminum coating.

d. Color pigments. A number of inorganic pigments provide color to paint. Titanium dioxide in both the rutile and anatase forms is the most popular white pigment because of its high refractive index and excellent hiding power (the ability to render a paint opaque). Rutile titanium has the highest refractive index and the best tinting strength of all other pigment types. (Tinting strength is the ease by which color pigments can be mixed with another pigment to color the paint.) Other pigments, both organic and inorganic, frequently are used in combination with titanium dioxide to add color. Natural iron oxides range in color from a yellow to a bright brown red, to a greenish brown, and a deep rich brown. Synthetic iron oxides range in color from yellow and red to brown and black. Red chromate pigments with sulfate, and sometimes molybdate additions, range in color from a light yellow to a bright orange or scarlet red. Because of their bright, clean color, lead chromate pigments frequently are used in highway striping paints and in safety color paints. Even though lead chromate is considered hazardous, the pigments in these paints will be difficult to replace because no other pigments have a similar light fastness and brightness. The purpose of organic pigments is primarily to provide paint color. Originally, organic coloring pigments were extracted as colorants from insects and vegetables. Synthetic organic pigments now have been developed, but few of these have technical or commercial importance in corrosion-preventative coatings. Compared with inorganic pigments, organic pigments generally are brighter colored, have less hiding, are more prone to bleed, have much poorer heat and light fast resistance, and are substantially higher in price. The most important class of organic color pigments are called azo pigments and are manufactured from aromatic hydrocarbons, which are available from coal tar or petroleum distillates. These pigments are characterized by the presence of a chromophore consisting of one or two azo groups (-N = N-).

e. Hiding pigments. Pigments with a high light refractive index provide the best hiding. Rutile titanium dioxide, followed by anatase titanium oxide, zinc sulfide, and zinc oxide have relatively high refractive indices. Conversely, silica, whiting, and barytes all have relatively low refractive indices and do not provide good hiding when formulated into paints.

f. Extender pigments. Certain types of pigments do not provide inhibition or have good barrier or sacrificial characteristics. They do not have a high refractive index and do not impart good color or hiding to a paint film. However, as reinforcing pigments and flow control pigments, they are important in coating formulation. As a class, these pigments can be called extender pigments because they are relatively inexpensive compared to most other pigments; they are used in conjunction with more expensive pigments to reduce costs. The use of extender pigments reduces shrinkage stresses within the paint film, giving it strength, and “extending” the pigment volume content at relatively low cost. Extender pigments include those based on carbonates, silicates, sulfates, barytes, and mica. Each of these types of pigments is somewhat different, but they all are relatively low cost materials that can be added in finely divided form to a paint to aid in its rheological properties (viscosity and flow control) and to reinforce the dry film strength.

4-7. Solvents

a. In a true sense, a solvent is defined as a substance, usually a liquid, that will dissolve and change a solid to a liquid state. In the coating industry, solvents are considered any volatile liquid formulated into a paint, even though it may not have solvency power. Some liquids are diluents and, even though the diluent may not have solvency power, it may enhance the solvency of other solvents in the paint. Water is the universal solvent, except for its use as a dispersant in emulsion coatings, but it is not used as a paint solvent in durable coatings. Water-soluble resins are susceptible to softening and swelling by water; therefore, coatings made from them will not be addressed in this manual. However, water-soluble resins should not be confused with water-emulsified resins, which were discussed earlier in this chapter. Organic solvents impart low water sensitivity and are the solvents of choice when dissolving solid resins.

b. The purpose of any solvent is to dissolve solid paint constituents, reduce viscosity, and render the paint fluid enough that it can be satisfactorily applied. The solvent is undesirable after application and must evaporate from the drying coating film. In addition to enabling application of the coating material, solvents must be able to wet the substrate being coated and penetrate into and help the coating seal any crevices, voids, or depressed irregularities. Also, the solvent must volatilize fast enough to prevent runs and sags in the drying coating film. However, a solvent that is too volatile can cause solvent pops, loss of gloss, dry spray, poor surface wetting and penetration, and poor film flow and inhibit cure. Virtually all coating formulations use a blend of solvents to achieve optimum properties. Some solvents within the blend will evaporate fast, enabling the drying paint to set quickly. Other solvents may dry slower and provide wettability and penetrability. Ultimately, all solvents should evaporate to allow the coating to achieve hardness, cure, and final properties. Solvents can be categorized according to their chemical composition. The most commonly used categorization subdivides solvents into classes called turpentines, hydrocarbons, ketones, esters, alcohols, and glycol ethers.

c. Turpentines. Turpentine solvents are actually hydrocarbon solvents; they are categorized separately because they are derived from southern pine trees as opposed to solvents fractionated from petroleum and coal tar refining. Turpentine is used infrequently today in manufacturing corrosion-protective coatings, although it is widely sold in retail paint stores for field thinning of oil-based house paints and varnishes. Gum-spirits turpentine is distilled from crude gum rosin obtained by tapping southern pine trees. Wood turpentine has a somewhat different composition from gum turpentine and is obtained by distillation of the crude rosin extracted from the ground wood from southern pine stumps. Sulfate turpentine is obtained as a by-product of the Kraft paper industry. Turpentine has good solvent power for most oil and oleoresinous binders, but its use is limited in modern paint technology because of its relatively high price and slow evaporation rate. Other turpentine-like solvents, such as dipentene and pine oil, also are obtained from southern pine trees and have specialized uses.

d. Hydrocarbon solvents. Hydrocarbon solvents are obtained from both petroleum and coal tar sources. Petroleum hydrocarbon solvents are the lighter (more volatile) fractions from the distillation of crude oil. Coal tar hydrocarbons are distillation products from coke oven by-products. Hydrocarbon solvents may be classified as aliphatic or aromatic.

(1) Aliphatic hydrocarbons. Aliphatic hydrocarbons are straight or cyclical carbon-hydrogen containing liquids that are nonpolar in character and exemplified by mineral spirits, “varnish makers and painters” (VMP) naphtha, and other materials such as hexane and heptane. For the most part, these solvents have poor to moderate solvency for all but oil-modified coatings. Their solvency can be increased by blending them with various amounts of other, more powerful solvents such as aromatic hydrocarbons or ketones. Aliphatic hydrocarbons are generally the least expensive of all solvents and can be obtained in a wide range of evaporating rates. Aliphatic solvents are considered the least toxic of any of the solvent classes, although—as with any other solvent—gloves, respirators, and protective clothing should be used by individuals applying paints containing these solvents. Naphthenic hydrocarbons are aliphatic hydrocarbon solvents, but with a cyclical ring molecular structure. The naphthenic solvents are midway between the aliphatic and aromatic solvents in solvency power. Naphthenic solvents are used in alkyd and epoxy ester coatings and asphaltic and coal tar-containing coatings.

(2) Aromatic hydrocarbons. Aromatic hydrocarbon solvents contain a benzene ring structure. The most common solvents of this type are toluene (toluol), xylene (xylol), and high-flash naphtha. Aromatic hydrocarbon solvents have a greater solvent power than aliphatic hydrocarbon solvents. They generally are good solvents for oils, oleoresinous binders, alkyds, bitumens (asphalts and coal tars), and some synthetic resins. Aromatic solvents can be blended with more powerful solvents to enhance their power of solvency.

e. Ketone solvents. Ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, and diacetone alcohol have varying evaporation rates and relatively strong solubility parameters. These solvents exhibit strong hydrogen bonding and high polarity. When retained in a paint film, they may attract and draw moisture into the coating. As with all other solvent classes, each of the ketone solvents has a different evaporation rate; care should be taken when using ketone solvents with slow evaporative rates to minimize solvent entrapment within the coating. As a class, ketones are polar materials characterized by exceptionally strong solvency for many resins used in protective coatings. They are used extensively as solvents for vinyls, urethanes, epoxies, and acrylics. Ketones usually are more expensive than ester-type solvents, but they are cost effective because the use of ketones allows for greater use of inexpensive aromatic diluents. As with all solvent families, solvency decreases as molecular weight and branching increase.

f. Ester solvents. Ester solvents contain the acetate functionality (-C-O-R). Ethyl acetate, isobutyl acetate, ethylene glycol, and monoethyl ether acetate are examples of ester solvents. They have solvency power between the aromatic hydrocarbons and ketones, but they have a high hydrogen bonding index and a relatively high polarity. Care should be taken to avoid solvent entrapment when using ester solvents. Ester solvents are strongly polar and are used as solvents for similarly polar resin film formers. The esters are characterized by a sweet, pleasant, strongly fruity odor. Ester solvents are used in cellulosic lacquers, urethanes, vinyl, epoxy, and acrylic coatings. Slow-volatilizing ester solvents are used as tail solvents in waterborne acrylic emulsions to aid coalescence and as tails in solvent-borne coatings to maintain solvency and reduce resin precipitation. Tail solvents are designed to be the last solvents to evaporate from a coating.

g. Alcohols. Alcohols are water miscible, and care should be taken when using them so water is not introduced into the coating. Alcohols are highly polar with a strong affinity for the water molecule. They are used to dissolve polar materials; and, when formulated into a coating, care should be taken to ensure that all alcohol will volatilize. Water miscibility and hydroscopisity are reduced as the alkyl group increases, and few alcohols above butanol (CyHgOH) have high miscibility with water. An exception is tertiary butanol, which—because of the compactness of the alkyl structure—retains complete water miscibility. The three most important alcohols are ethanol (denatured), isopropanol, and n-butanol. Methanol is toxic and is used only as a polar additive in paint removers because its low molecular weight serves it well as a penetrant. Alcohols are used as solvents for resins such as polyvinyl acetate, some phenolics, vinyl butyral wash primers, most epoxies, and inorganic zinc-rich coatings based on ethyl silicate vehicles. Because of reactivity of the alcohol hydroxyl group, alcohol solvents cannot be used as solvents in polyurethane coatings. Alcohol is a solvent common to many epoxies. Chlorinated solvents such as 1,1,1, trichloroethane, chloroforms, dichloroethane and dichloroethylene, and methylene chloride, although used infrequently in paints, are good paint strippers, especially for epoxies and polyurethanes. Chlorinated solvents are nonflammable and VOC compliant because they generally are nonphotochemically reactive. However, they are toxic to humans and are environmental contaminants. These solvents should not be stored in, or used with, aluminum containers or equipment.

h. Glycol ether solvents. Glycol ether solvents, such as ethylene glycol monoethyl ether and ethylene glycol monobutyl ether, are a specific subcategory of the ester solvents. The most important solvent of this type has been ethylene glycol monoethyl ether (Cellosolve®[1]) acetate. However, because of toxologic considerations, this solvent largely has been replaced by propylene glycol monomethyl ether acetate, which appears to be less toxic. Glycol ethers are tail solvents for epoxies, vinyls, and urethanes. Glycol ether solvents are water-miscible and will attract moisture in buried or immersion conditions; therefore, care must be taken to ensure they completely volatilize from coatings to be used in immersion or below grade service. Anhydrous solvent grades are necessary if glycol ethers are used in urethane formulations. Glycol ethers are particularly good solvents for epoxy resins.

i. Solvent safety. Safety should be a consideration at all times when using solvents because all solvents are combustible and some are highly flammable. Solvents with lower molecular weight or faster evaporating rates usually are more flammable. Fast volatilizing, flammable solvents can lead to explosions, especially within confined spaces. All solvents are heavier than air and tend to flow downward; so, unless adequate ventilation and air movement are used, solvent vapors will collect and concentrate in low-lying spaces. Safety considerations are discussed in detail in Chapter 10.

4-8. Miscellaneous Additives

A number of miscellaneous compounds are added by the paint formulator to paints for specialized purposes. These include antiskinning agents, fungicides, thixotropes, UV light absorbers, plasticizers, flow agents, and emulsion aids.

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[1] Union Carbide, Indianapolis, Indiana.

a. Antiskinning agents. Skinning sometimes occurs on storage of coatings containing drying oils. The surface of a paint dries and forms a skin on the paint surface in the can. When used excessively, driers have a tendency to aggravate skinning. To avoid skinning, antioxidants such as certain phenols and oximes can be added. The oximes, characterized by the reactive group (-C=N-OH) are by far the most commonly used antiskinning agents. Skinning is the result of the drier functioning properly, and it usually is not a problem in unopened or full cans. Antiskinning agents are volatile and accordingly, when using some of the paint in a can, close it tightly after use.

b. Fungicides. Fungicides or mildew inhibitors are added to paints to prevent mold growth. Mildew feeds on some components of a paint film, particularly oleoresinous vehicles, most latex paints, and some polyamide epoxies that offer a source of food. Mildew spores are omnipresent in air, will deposit on the paint, and, under the right conditions, will begin to grow. In the past, compounds based on phenyl mercuric and tributyl tin compounds were used as fungicides; but, because of their high toxicity, they have been replaced by complex organics such as carbamates, benzothiazoles, alkylisothiazolinone, chlorinated isophthalonitriles, and chlorinated adamantane complexes. However, the new materials have not attained the effectiveness of the older materials. Fungicides function in the can to kill organisms that might upset paint stability, which is particularly important in latex emulsion paints that can become rancid if microbiological growth is not stopped.

c. Thixotropes. Rheological coating properties such as film build, sag control, flow and leveling, and pigment settling properties can be adjusted through the use of thixotropic additives. Thixotropes can enable a rapid increase in the viscosity of a liquid coating material and allow it to build thicknesses over edges and plane surfaces and to resist sag. However, when mixing and applying the coating, shear stresses can break down the coating thixotropy rapidly, enabling it to be applied as if it were low in viscosity. Thixotropy recovers after application, and film build and antisag resistance again occur. There are a number of thixotropes that can be added to solvent-borne coating systems, including castor oil derivatives, high molecular weight polyolefins, montmorillonite and other clays, fumed silicas, fibrated minerals, calcium sulphonate derivatives, and others. Each of these classes has specific advantages and disadvantages with each of the binder systems in which they are incorporated. Similarly, thixotropes are important for waterborne systems to provide the same properties. The more common waterborne system thixotropes are nonionic cellulosic thickeners, polyacrylic acids and salts, anionic polycarboxylic acid-based thixotropes, and, more recently, a nonionic associative thickener based on ethoxylated polyether-based urethane block copolymers. The nonionic thickeners give the most improved flow and leveling characteristics to water emulsion coatings, providing better gloss and semigloss paints. In roller applications, the nonionic thickeners result in a significantly reduced roller spatter. Thixotropes prevent hard settling of many heavy pigments, such as zinc. Most thixotropes deteriorate on aging, which causes variations in viscosity of the paint in the can. Some paints have increased viscosity; others may suffer a viscosity decrease.

d. Flow agents. The addition of flow agents enhances the freshly applied paint film's ability to flow out after application, eliminating brush marks, roller patterns, orange peel from spraying, and other film irregularities and defects. The flow rate of paint is affected by the rate of solvent release and solvent system evaporation. Surface tension and the coating’s viscosity, which vary as a function of temperature, also affect the rate of flow or leveling of the applied paint film. Depending on the type of flow problem encountered, the generic type of coating, and the coating formulation, different flow and leveling agents are added in small amounts (usually less than one percent) to eliminate or minimize problems. Most flow agents function by increasing the viscous force in the coating, overcoming the paint's tendency to flow. Surfactants also help to overcome leveling problems by reducing surface tension.

e. Emulsion aids. Emulsion aids are used in waterborne paints and often are called surfactants. Proper use of surfactants enable a waterborne emulsion to remain in suspension and keep it from settling and packing at the bottom of a can during prolonged storage. All surfactants have a hydrophilic (water-loving) group and a hydrophobic (water-hating) group, which is water repelling. The hydrophobic group is usually in the form of a long hydrocarbon tail terminating in a simple long polar alkyl group. The hydrophilic group is usually a charged species such as an ammonia ion, a polar organic group (carboxylic acid), hydroxyl, sulfate, etc. The surfactant molecules containing both the hydrophobic and hydrophilic ends orient themselves around the emulsion particles to effectively separate them and keep them apart. However, prolonged storage at elevated temperatures, or freezing the emulsion, may destabilize it and cause separation and possible de-emulsification. A number of different types of surfactants can be used, depending on cost, solution, pH, and specific emulsion requirements. Emulsion chemistry is complex and, unlike formulating solvent-based paints, often requires considerable trial and error.

f. UV absorbers. UV light, particularly in the actinic region of 280 to 315 nm, can degrade exterior paint films. Incident UV light is absorbed by the paint, raising the paint to a higher energy state. This causes bond cleavage and release of free radicals, which leads to depolymerization, chain scission, or, in some instances, crosslinking and embrittlement. This surface effect ultimately results in degradation of the coating at either the surface (as is generally true with epoxies that readily chalk) or the coating interior, if the coating is partially transparent to UV light energy. To prevent this, UV absorbers are added to the formulation at the rate of approximately 1 to 3 percent, by weight, depending on the type of coating, the degree of pigmentation, and the type of surface. Zinc oxide is an effective UV absorber, but it sometimes leads to embrittlement of oil-based coatings and may not be appropriate for other generic types of coatings. Most UV light absorbers are complex substituted aromatic compounds that absorb UV radiation strongly without being degraded. Hydroxy substituted benzophenones and benzotriazoles are used most commonly.

g. Plasticizers. Plasticization is a process of increasing the flexibility and adhesion of an organic coating film and decreasing its brittleness, cohesiveness, and glass transition temperature (the temperature at which a polymer changes from a flexible, rubber-like material to one that is hard and brittle). Plasticization can be achieved by chemically modifying the resin polymer or by adding compounds to the coating formulation. Chemical modification of the compound can be done by reducing crosslinking or by formulating resin molecules with bulky side chains to prevent parallel orientation and crystallinity. Alternately, external plasticizers (such as monomeric phthalates, phosphates, adipates, and septacates), chlorinated paraffin, or biphenyls can be added to a resin system to soften it and lower the glass transition temperature. The plasticizing materials generally are relatively low molecular weight, slow-evaporating materials that, when mixed with a resin, soften it by preventing crystalline orientation and terminating crosslinking sites. The type of plasticizing agent used depends principally on the generic type and molecular weight of the resin system used in the coatings formulation. In time in some applications or service conditions (such as high temperature/humidity), low molecular weight plasticizers may migrate to the surface of the coating; and the surface may become sticky and attract and hold dirt. More importantly, the coating often embrittles, becomes less flexible, or shows surface or through-cracking.

4-9. Zinc-Rich Coatings

Zinc-rich coatings, or zinc-rich primers, are unique in that they provide galvanic protection to a steel substrate. As “rich” in the name implies, the binder contains a large amount of metallic zinc dust pigment. The binder can be an inorganic zinc silicate or an organic resin such as an epoxy, butyl, or urethane. After the coating is applied to a thoroughly cleaned steel substrate, the binder holds the metallic zinc particles together and in contact with the steel. Thus, metal-to-metal contact of the two dissimilar metals is made and results in a galvanic cell. Zinc becomes the anode in this cell and sacrifices itself to protect the underlying steel cathode. Properly applied zinc-rich coatings, zinc galvanized coatings, and thermally sprayed zinc eliminate pitting and under-film corrosion even at voids, pinholes, scratches, and abrasions in the coating system. This cannot be said of any other type of coating, and this protective capability makes zinc-rich coatings unique and widely used (refer to Chapter 2).

a. Inorganic zinc-rich binders. All inorganic zinc-rich coatings require an extremely clean surface (SSPC-SP 10 or SP 5), or application over a clean, pickled surface. Because of their inorganic nature, inorganic zinc-rich coatings are highly resistant to scuffing, scraping, and mechanical damage. They have good dry heat resistance to temperatures as high as 399 °C (750 °F) and good resistance to immersion in oil, petroleum distillate products, solvents, fresh water, and many other neutral pH aqueous solutions. Some formulations are suitable for immersion in salt water; others are not. The high conductivity of salt water enhances corrosion of both the zinc and zinc pigment particles within the coating and the underlying steel. Therefore, the protective life of zinc-rich coating in saltwater immersion may not be as long as that in freshwater immersion. In atmospheric environments, inorganic zinc-rich coatings provide long-term corrosion protection in damp, humid environments and where chemical attack does not occur. Inorganic zinc-rich coatings can be applied to steel at thicknesses of from 0.05 to 0.09 mm (2 to 3.5 mils) to provide atmospheric and immersion corrosion protection and left without a topcoat for long periods of time. Salt contamination may be a problem in marine environments; and research and panel testing done by NASA have established that zinc-rich primers, particularly inorganic zinc-rich primers, protect longer without topcoats than the same primers with an organic topcoat. However, other studies for chemical and weathering environments have established that topcoating with an organic topcoat may increase coating system longevity. Both inorganic and organic zinc-rich coatings can be specially formulated as preconstruction primers. This type of primer is applied to ships, subassemblies, and other prefabricated steel. When the steel is fabricated, welding can be done without removal of the preconstruction zinc-rich primer. Topcoating inorganic zinc-rich coatings may be more difficult than with any other coating because of the inherent porosity of the zinc primer. The binder partially wets and adheres the zinc-dust particles together and to the underlying substrate, but it does not fully encapsulate or seal the surface. Therefore, topcoats applied over the porous surface may displace entrapped air causing pinholes, bubbles, or voids within the topcoat cross-section. This problem is not nearly as prevalent when using organic zinc-rich coatings because the organic binder more thoroughly wets, encapsulates, and seals the porosity of the highly zinc-dust-loaded dry film. Inorganic zinc-rich coatings may be one of three major groups: post-cured water-based alkali metal silicates, self-cured water-based alkali metal silicates, and self-cured solvent-based alkyl silicates.

(1) Post-cured, water-based alkali metal silicates. Post-cured, water-based inorganic silicates come as a three-package system: zinc dust, silicate binder, and curing solution all packaged separately. The binder is an inorganic alkali metal silicate, usually of the sodium, potassium, or lithium family. Zinc powder is slowly mixed into the alkali metal silicate binder, and the resulting solution is spray applied with an agitated spray pot to keep the zinc-dust pigment in proper suspension. After water evaporation and hardening of the zinc silicate coating, a phosphoric-acid-based curing solution is sprayed or brushed over the surface to neutralize the alkali metal binder. The neutralization reaction and subsequent interactions with zinc and iron ions further neutralize the silicate alkalinity and insolubilize the film. The coating becomes insoluble to water and resistant to weathering exposure. Post-cured, inorganic zinc-rich-coatings are believed to be the best performing of the inorganic zinc-rich coating materials because of their relatively complete, insolubilized, hard cure attained after application of the curing solution.

(2) Self-cured, water-based alkali silicates. The most common of these silicate binders is based on potassium and lithium silicates, or combinations. Lithium hydroxide-colloidal silica and quaternary ammonium silicate binders also can be used. The alkali silicate binder is partially dehydrolized so its high alkalinity is considerably reduced in comparison with post-cured, inorganic silicate vehicles. Therefore, after application, initial water evaporation, and insolubilization, sufficient neutralization and cure are attained by further reaction with atmospheric moisture and carbon dioxide. Carbon dioxide in the presence of atmospheric moisture forms a weak carbonic acid, which in time is sufficient to neutralize the alkalinity of the silicate binder. If a more rapid insolubilization or cure is desired, heat or an acidic curing solution can be applied. When final curing is attained, most water-based, zinc-rich coatings—whether post- or self-cured—experience a color change, usually from a reddish or light gray to a darker blue-gray.

(3) Self-cured, solvent-based alkyl silicates. The binders for these silicate coatings consist essentially of partially hydrolyzed alkyl silicates of the series methyl through hexyl or glycol ether silicates. Of these, the ethyl silicate type is the most prevalent. After application and initial solvent drying, the coating system hardens; but to cure, hydrolysis with moisture from humidity in the air is required. The hydrolysis of the silicate binder liberates ethyl alcohol (or an alkyl alcohol if other alkyl silicates are used). The alcohol volatilizes, makes the hydrolysis reaction irreversible, and hardens and cures the binder. If the silicate binder is applied indoors or in an arid exterior environment, water may be sprayed onto the surface with a spray gun or a garden hose with a fine atomization. Two or three applications may be required over a 2- or 3-day period to obtain optimum curing of the binder. All inorganic zinc-rich coatings can attain VOC compliance because of their high solids content, but the water-based post- and self-curing alkali silicates have virtually no VOC release.

b. Organic zinc-rich binders. Organic zinc-rich coatings most commonly are formulated from epoxy polyamide, urethane, vinyl, and chlorinated rubber binders. Alkyds have been used for some air-dry formulations, but they most commonly are used with baking formulations, notably in the automotive industry. Drying, hardening, and ultimate curing of the organic zinc-rich coating is determined by the type of binder used. The hardening and curing mechanisms of the various organic binders have been described previously (paragraphs 4-2 and 4-3) and are the same for organic zinc-rich coatings. The major difference is that, with organic zinc-rich coatings, the pigment is zinc dust in high concentrations to attain a dry film pigment volume of 75 percent or greater. This high zinc loading enables the organic zinc-rich coatings to provide galvanic sacrificial protection. The zinc-dust particles within the coating system must be in electrical contact with the thoroughly cleaned, underlying steel surface, and the zinc-dust pigment particles must touch each other for galvanic protection. Usually when formulated into organic vehicles, the binder more thoroughly encapsulates the zinc and reduces the sacrificial capability of the applied film. However, this encapsulation does not prevent galvanic protection by organic zinc-rich primers. In fact, the encapsulation of the organic binder makes organic zinc-rich coatings more tolerant of deficient surface preparation because the binder more readily wets and seals the prepared surfaces where residues of rust or old paint may remain. Also, topcoating with the same generic type of topcoat (e.g., a polyamide epoxy zinc-rich topcoated with a polyamide epoxy topcoat) is more easily accomplished because organic zinc-rich coatings have a less porous surface and are more similar to conventional organic coatings than the inorganic, zinc-rich coatings.

(1) Organic zinc-rich coatings frequently are used to touch up and repair inorganic zinc-rich coatings because the wettability of the organic binder provides better adhesion to

the inorganic surface than another coat of inorganic zinc-rich coating. Organic zinc-rich primers generally are considered to be easier to apply by spray than inorganic zinc-rich coatings, and they are somewhat more tolerant of poor surface preparation because of the wettability and penetrability of the organic binder. Organic zinc-rich coatings have less of a tendency for mud cracking at excessive thicknesses (over 0.13 mm [5 mils]) and are easier to topcoat than inorganic zinc-rich coatings; however, they do not have the heat and abrasion resistance of the inorganic zinc-rich coatings. Organic zinc-rich coatings do not provide the same long-term corrosion protection to steel as most inorganic zinc-rich coatings.

(2) The VOC characteristics of organic zinc-rich coatings are similar to those of the nonzinc-dust-pigmented binders. Organic zinc-rich coatings are highly pigmented, but this does not substantially reduce VOC because the pigment has a high specific gravity and is dense relative to its volume. Generally there is less organic binder per gallon of organic zinc-rich paint, and VOC emissions are slightly less than for nonzinc-rich-pigmented coating systems using the same binder.

(3) Properly applied zinc-rich coatings, zinc galvanized coatings, and thermally sprayed zinc eliminate pitting and under-film corrosion even at voids, pinholes, scratches, and abrasions in the coating system. This cannot be said of any other type of coating, and this protective capability makes zinc coatings unique and widely used. The binders of zinc-rich coatings can be organic or inorganic.

4-10. Volatile Organic Compounds

VOCs are in most protective coatings. Common paint solvents such as aromatic hydrocarbons, aliphatic hydrocarbons, ketones, acetates, and alcohols are photochemically reactive. On evaporation into the atmosphere, these paint solvents react with nitrous oxides (combustion compounds from automotive emissions and burning of fuels) and sunlight to form ozone and air pollutants. In the 1960s, air pollution problems usually were handled by state and local agencies. There was no national goal to address air pollution. In the 1970s, Congress passed the Clean Air Act and established the U.S. Environmental Protection Agency (USEPA). The Clean Air Act gave USEPA the responsibility of identifying the most serious air pollutants and setting national air qualities standards for each. Ozone was at the top of the list. The air quality legislation was an attempt to reduce levels of ozone and other air pollutants. Rules limiting the amount of VOCs in paint have been established since then, but they vary from state to state and even regionally within a given state. Such variability in laws regarding VOC emissions has been of considerable concern to many coating manufacturers whose products are sold nationally. A particular coating material may comply with the laws of one state but not with those of another state. Even within a given state, the coating may be legal in most areas but illegal in certain cities or regions. For years the coatings industry has pushed for national VOC legislation that will supersede and pre-empt local legislation regarding VOC emissions. However, national VOC legislation has not been enacted, and permissible VOC emissions vary widely, depending on the generic type of coating and the location where it is applied. VOC compliant coatings are formulated principally by increasing the percent volume of solids, chiefly by minimizing solvent content, use of relatively high volume low density pigments, and the use of lesser amounts of stronger solvents. Additionally, the alkyd resin is combined with other synthetic resins (such as epoxies, phenols, and urethanes) and results in a more reactive higher solids coating system. Straight alkyd systems currently are formulated with VOCs of 350 g/L (2.9 lb/gal) or higher. Future formulations probably will require a VOC as low as 250 g/L (2.1 lb/gal). Chapter 11 discusses VOC regulations in detail.

4-11. Powder Coating

Powder coatings are made by mixing resins, pigments, and additives together and heating them to form a melt. The melt is extruded, cooled, and broken up by milling to produce a powder with a particle size distribution of approximately 10 to 100 µm. The article to be coated usually is preheated to 204 to 260 °C (400 to 500 °F), depending on the powder to be applied. The pigmented powder is applied, either by immersing the article in a fluidized bed of the powder (which is kept mobile by the passage of air through it) or by electrostatic spray guns. After application, the article being coated is heated to the melting point of the powder so the powder flows together. The powder can be thermoplastic or thermosetting. With thermoset powders, crosslinking agents also are made into a powder, and this powder is applied at the same time as the base powder. After application, crosslinking occurs on melting. Epoxy powder coatings are by far the most popular, although polyester, polyurethane, acrylic, and other resin types can be used.

a. Powder coatings do not readily give satisfactory films at thicknesses below approximately 0.05 mm (2 mils); they require special application and heating equipment. Powder coatings form good-looking, thick, tough coatings that contain no solvent. Because they are VOC compliant, they comprise a technology that is of considerable interest in the protective coatings area. Currently, powders are used mostly in the coating of relatively small items that can be easily heated to the melting point of the powder being applied. Fusion-bonded powder coatings are applied to preheated pipe surfaces with or without primers. The coating usually is applied 0.30 to 0.63 mm (12 to 25 mils) thick for aboveground pipe installations to eliminate chalking and to maximize surface life; topcoating frequently is done with a urethane coating system.

b. Thermally sprayed organic powders have been applied to structural steel and other large metal objects. The process is expensive and adhesion sometimes is a problem because the large item being coated does not attain a uniformly high substrate temperature when heated; and the applied powder, even though in a liquid “melt,” does not have good surface wetting properties. Current furnaces or heating ovens are large enough to handle concrete reinforcing rods, small- to medium-diameter pipe, small structural steel pieces, and sheet piling.

c. Although of considerable interest to the protective coating industry, powder coating has not been used commercially to protect large steel surfaces or heavy, massive structural steel shapes.

4-12. Thermal Spray

a. Thermal spray coatings consist of a process by which an organic powder or metal wire is melted and spray-deposited onto a surface. In the past, metallizing was the term used to describe wire flame spraying. However, because of dramatic improvements in equipment used to heat and spray the molten metal and nonmetallic polymers onto a surface, the term thermal spraying is more descriptive. Thermal spraying is a process by which a finely divided molten metallic or nonmetallic material is sprayed onto a prepared substrate to form a coating. The sprayed material is originally in the form of a wire or powder. The thermal spray-gun heats the wire or powder to a molten or plastic state, and compressed air or gases propel it to the surface being coated and deposit it into a film. Refer to CWGS 05036.

b. Zinc, aluminum, and their alloys are the most widely used metals for thermal spray, corrosion-resistant coatings. These metals provide excellent protection in a variety of marine and industrial environments. After spray application, zinc is anodic to an underlying steel surface. Because of its aluminum oxide coating, aluminum exhibits galvanic protection for only a short period of time. Afterward, the oxidized aluminum coating functions principally as a barrier coat. In general, aluminum corrodes less rapidly than zinc in highly acidic conditions, but zinc performs better in alkaline environments. Zinc frequently is the preferred metal for protection of steel in fresh cold waters, although aluminum also is suitable. Aluminum is preferable for aqueous solutions above 60 °C (140 °F).

c. Organic sealers or topcoats commonly are used over the thermally sprayed metal to extend the life of the system and provide color for decorative purposes. Common sealers include many of the synthetic resin coating systems, especially vinyls, epoxies, polyurethanes, and phenolics. Sealers are essential for most immersion or severe chemical corrosion applications. Most sealers are applied in at least two coats, the first thinned for penetration into the porosity of the thermally deposited metal coating. The second and sometimes third coat of a sealer are applied unthinned as build coats.

d. Because there are no solvents or volatile material in any metallic thermal spray system, VOC compliance is not a problem. However, VOC compliance may depend on the organic sealer coating used.

e. An advantage of the thermal spray system is that essentially no startup or cleanup procedures are involved. The wire or powder feed stock is fed to the spray gun, the heat source is ignited, and spraying of the molten feed stock begins. On conclusion of thermal spraying, the device is shut off, and the process stops, with virtually no equipment cleanup required.

f. Blast cleaning surface preparation to a clean white metal, preferably with an anchor profile exceeding 0.08 mm (3 mils) is required for any thermal spray coating. Thermal spray metal (and plastic) coatings have little wetting ability at the time of application so cannot penetrate, seal, or encapsulate any contaminates on the surface to be coated. On cooling after application, the metal particles undergo a thermal contraction that applies a shrinkage stress to the metallic film. A minimum anchor pattern of 0.08 mm (3 mils), and preferably 0.10 to 0.13 mm (4 to 5 mils), is required to withstand the shrinkage stresses and to dissipate these stresses over a greater interfacial area between the applied metallic film and the underlying steel substrate.

g. The common methods of thermospray are:

(1) Wire flame spraying. Acetylene or other common fuel gases are combined with oxygen and ignited in the spray gun. A wire—usually zinc, aluminum, or zinc-aluminum alloys but sometimes nickel, stainless steel, or another metal—is fed through the flame, is melted, and is deposited on the surface. Wire flame sprayed coatings generally exhibit lower bond strengths, higher porosity, a narrow working temperature range, and a higher heat transmittance to the substrate than plasma or electric arc spray coatings.

(2) Powder flame spraying. A common fuel gas is used with a metal or plastic powder. The powder is stored in a hopper mounted on top of a spray gun, and a small amount of oxygen is diverted from the gas supply to carry the powder by aspiration into the oxygen-fuel gas flame. The melted powder is carried by the flame to the object being coated. An air/propane mixture is used for polymer powders. The object to be coated must be preheated to at least 79 °C (175 °F) prior to the spray application of the polymer powder. Because of the lower particle velocities obtained, the coatings generally have a lower bond strength, a higher porosity, and a lower overall cohesive strength than the coatings produced by any of the other thermal spray methods. The bond strength and other film properties can be improved considerably by preheating the substrate to 49 °C (120 °F) or more prior to application of the powder.

(3) Electric arc spraying. The spray gun used in electric arc spraying uses two feed stock wires as electrodes. An electric current is applied across the wires so that an electric arc is formed at the intersection. Heat from the electric arc melts the wires, a stream of compressed air flows across the arc zone, and the melted metal is removed from the wires and propelled to the surface. Because of the high temperatures in the arc zone, the coatings have excellent adhesion and high cohesive strength. Super heating of the particles after impact may lead to a metallurgical “weld” bond with some metals, substantially increasing adhesion and cohesive strength.

(4) Plasma spraying. Plasma is a hot gas issuing from the spray gun; it resembles a bright flame and is created by passing inert gas through an electric arc within the gun. The arc heats the gas to temperatures well above the melting point of any known substance. Powder feed stock is introduced into and melted by the plasma stream that also carries the molten metal to the work piece. The plasma system produces excellent quality coatings, but the equipment is complex, expensive, and difficult to operate. Plasma spraying is used when coatings are needed to provide the utmost in corrosion protection against chemical or high temperature corrosion, and when the work can be done in a shop environment.

4-13. Galvanizing

a. Hot dip galvanizing is the process by which a zinc protective coating is applied to steel by immersing an object in a molten zinc bath. Prior to immersion in the zinc bath, contaminants on the steel must be removed. Oil, grease, and other surface deposits are removed by immersing in a hot water detergent solution prior to pickling, steam cleaning, or steam-detergent cleaning the steel. The steel surface also must be thoroughly cleaned of mill scale and rust. This is usually done by sulfuric acid or phosphoric acid pickling. The steel to be galvanized is immersed in a hot acid bath. The hot acid aggressively attacks the steel surface, cleaning, etching, and roughening it. After continuous strip or batch pickling, the steel is water-rinsed or dipped to remove acid residues prior to immersion in the molten zinc galvanizing bath. The immersion in molten zinc may be done by one of two methods: continuous or batch processing. Sheet steel may be hot dipped by continuously passing the metal through a molten zinc bath. Continuous processing is highly automated and often is associated with steel mill operations. Batch processing generally is performed on fabricated items that range in size from large structural steel objects to small items such as nuts, bolts, and fasteners. With batch galvanizing, the objects are submerged into the molten zinc bath, held there for a suitable time, then removed.

b. A major advantage of galvanizing is that the zinc coating alloys itself with the steel. The extent of the alloy is a function of the heat of the zinc bath (the bath is generally maintained at a range of 443 to 460 °C [830 to 860 °F]) and the amount of time the steel is submerged in the bath. The greater the submersion time, the greater the extent of the iron-zinc alloying. The item being galvanized must be at the bath temperature for optimum galvanizing adhesion. This, however, has two disadvantages. The object being coated must not undergo any undesirable property changes at the temperature required for galvanizing. Also enclosed or sealed cavities in the object being galvanized (particularly with hot dip batch galvanizing) must be avoided by design or be opened by drilling to provide a vent hole to allow release of entrapped air that will expand when heated in a galvanizing bath.

c. Corrosion protection afforded steel by galvanizing is greater than that provided by thermal spraying zinc-rich or organic coatings of similar thicknesses. This is a result of the smooth, continuous nature of the zinc coating deposited during the hot dip process and the iron-zinc alloying that occurs at the interface between the zinc coating and the steel surface. For small steel objects, grating, small-diameter piping, conduit, and other configurations with a high surface area-to-weight ratio, galvanizing is preferable to painting and thermal spraying because immersion in a molten zinc bath readily coats all surface areas quickly and economically. Conversely, when coating thick, heavy steel objects with a relatively low surface area-to-weight ratio, thermal spraying and/or painting may be more economical.

d. Although almost any steel can be galvanized, steel chemistry can dramatically affect the thickness, structure, and appearance of the galvanized coating. Silicon, phosphorus, carbon, and manganese may be present in steel and affect the galvanizing properties. The most influential steel constituent affecting galvanizing is silicon, which is added to steel as ferro-silicon to remove oxygen from the molten steel before casting. In high silicon steels, an undesirable increase in coating thickness occurs because of the accelerated growth of the zinc-iron alloyed layers. This growth is caused by the formation of loosely packed small grains or crystals in the outermost alloy layer of the coating that allows zinc from the bath to penetrate to the steel surface. In general, steels with the following maximum impurity levels are best suited to galvanizing: 0.05 percent silicon, 0.05 percent phosphorus, 0.25 percent carbon, and 1.3 percent manganese.

e. Hot dip galvanizing has a number of advantages, including the ability to coat recessed or difficult-to-coat areas (such as corners and edges) with a sufficient coating thickness. Also because the coating is metallic and metallurgically combined with the steel, it has good abrasion and corrosion resistance. When coating steel with a large surface area-to-weight ratio, galvanizing is much more economical than painting because galvanizers charge by the weight of the object being galvanized and painters charge by the square foot of surface area of the object being painted. A major disadvantage is that the hot dip process is not portable, and the object being coated must be taken to the zinc-coating facility for galvanizing.

f. Hot dip galvanizing causes no significant alteration in the bend, tensile, and impact properties of galvanized steel, so steel strength and ductility are unaffected. Welded structures have higher strength when galvanized than when uncoated because hot dip galvanizing reduces weld stresses by 50 to 60 percent. For most steels, little reduction in fatigue strength occurs as a result of galvanizing. Steel does not embrittle as a result of hot dip galvanizing. Hydrogen embrittlement does not occur when ordinary carbon or low alloy steels are galvanized. Hardened steels may become embrittled if the hydrogen picked up during the pickling cleaning operation is not expelled during immersion in the molten zinc bath. Steels of medium to high strengths that have been severely cold worked may have local areas susceptible to hydrogen embrittlement. As a rule, however, hydrogen embrittlement as a result of cold working is not a problem for steel subject to hot dip galvanizing.

g. Coatings can be successfully painted immediately after galvanizing or after extended weathering. A white rust-preventative oil or wax may be applied to the galvanized surface to prevent the formation of zinc-corrosion products such as zinc hydroxides, oxides, and carbonates that result in a white discoloration on the galvanized surface. If painting is to be done immediately after galvanizing, check to ensure that a rust preventative has not been added. The freshly galvanized surface should be roughened slightly by light brush blast cleaning or mechanical means. Alternatively, vinyl butyral wash primers or other pretreatment primers can be applied that will etch and adhere to the underlying galvanized surface.

h. If coating after weathering, the galvanized surface will be eroded by zinc corrosion and the formation of insoluble zinc-corrosion products. The zinc corrosion roughens the galvanized surface and frequently no further mechanical roughening or brush blast cleaning is required. However, care should be taken to ensure that all loose zinc-corrosion products are removed by scrubbing or power washing the surface prior to painting. Wash primers, or primers specially formulated for application over galvanized surfaces, frequently are preferred.

i. Galvanized steel can be topcoated with any nonsaponifiable alkali-resistant paint. Zinc dust, zinc oxide-containing paints are particularly recommended, as are zinc-rich coatings. Water-based acrylic latex emulsions, epoxies, vinyl copolymer paints, and chlorinated rubber and coal tar epoxy coatings all have been applied with good success over properly prepared galvanized steel surfaces.

4-14. Tapes and Wraps

a. Protective tapes and wraps are used almost exclusively for protecting pipelines and tubular structural shapes from below-grade or (underground) corrosion. Cathodic protection is used in many situations to supplement corrosion protection. The tape or wrap must provide a barrier resistance to the below-grade environment, have good adhesion, and be able to act as an effective electrical insulator to aid in effective cathodic protection.

b. A tape is a composite material consisting of at least two layers. The first or innermost layer is usually a soft, elastomeric material formulated to adhere to an underlying substrate. The substrate can be either primed bare metal or another tape layer. The tape backing or outer layer is a monolithic polymeric material designed for tensile strength, mechanical strength, temperature, and electrical resistance. Typical tape backings include polyvinylchloride, polyethylene, polyolefin, butyl, ethylene propylene diamine monomer (EPDM), and, occasionally, nylon or glass fibers. Adhesives are usually butyl rubbers or butyl chlorinated rubbers but can be petrolatum and petrolatum wax compounds.

c. The tapes can be cold applied, hot applied, and cold applied with subsequent heat application as a heat-shrink material. Multilayered tapes frequently are used on a pipeline by applying a one-tape system then overcoating it with a different tape system. When this is done, the inner layer is designed primarily for corrosion protection, and the outer layer is designed to resist moisture, soil stresses, UV light, or other environmental influences.

d. Most tape systems are applied over a blast-cleaned surface, usually SSPC-SP 6 or better. This standard generally is a requirement for all adhesives except those based on petrolatum wax, which can be applied over a lesser prepared surface because of its wettability and softness. Most tapes perform better when applied over a primer, which commonly is an epoxy. The primer provides a bonding surface for best adhesion of the subsequently applied tape coatings.

e. Tape systems are applied by hand or, preferably, by a hand-assisted tape wrapster that is pushed and pulled around a pipe by as many as four or five workers per machine. Powered wrapsters provide the best application and allow for a more constant tension, uniform overlaps, fewer wrinkles, and a lesser clearance underneath the pipe (as little as 304.8 mm [12 in.]). Tape wrapping machines are available that will simultaneously apply two tape layers to a pipe. These tape wrapping machines are most useful for over-the-ditch applications.

f. For tape applications in the pipe mill or fabricating shop, surface preparation by blast cleaning is the most common, usually to an SSPC-SP 10 quality. Application of a primer and two or more tape layers applied by automatic pipe-coating equipment under constant tension of 10 to 14 psi results in a tight, wrinkle-free coating. The coating is inspected by automated high voltage holiday inspection (minimum 6,000 V). After mill application of a tape system, careful handling is required to avoid damaging or stripping the applied tape system.

g. In the pipe mill, hot-applied plastic tapes also have been used. The pipe surface is cleaned to an SSPC-SP 10 and heated to approximately 121 °C (250 °F) to melt the tape adhesive to provide a good bond. Mill-applied tape coating systems require careful handling and installation, and over-the-ditch application eliminates the need to repair shipping and handling damage. However, over-the-ditch application generally is more labor intensive and is subject to weather variables and adverse application conditions. During installation of any pipeline system—whether coated by a tape wrapping system, fusion bonded system, or extruded high density polyethylene wraps—care is necessary during backfilling operations to prevent rock and stone damage and impact into the coating. Insulating mats and/or blankets are sometimes wrapped around a pipe to prevent backfilling damage or, alternatively, specially conductive backfilling earths are initially placed around the pipe layer prior to filling the ditch. Another tape system, extruded polyethylene, is relatively new and is gaining acceptance in the United States. This coating system generally consists of blast cleaning to SSPC-SP 6 followed by the application of an epoxy primer to approximately 0.05 mm (2 mils) dry film thickness. The pipe then is heated to approximately 135 °C (275 °F) and approximately 0.20 mm (8 mils) of a polyethylene copolymer adhesive is extruded around the pipe, followed by 3 mm (118 mils) of a polyethylene outer wrap extruded spirally over the adhesive. The preheating melts the adhesive and provides wetting capability. Additionally, the polyethylene extrusion to the hot pipe shrinks to form a tightly adhered, thick, seamless coating with high resistance to mechanical damage, moisture permeation, and UV light.

h. During pipe-laying operations in the field, the joints must be protected by application of paints or protective coatings or, more commonly, a tape wrapping system.

(1) Polyvinyl chloride tapes. Tapes with a PVC backing can be used with a variety of adhesive materials, including butyl rubber and petrolatum wax. The greatest advantage of PVC-backed tapes is that they have an ability to conform to regular substrates and provide a good barrier to penetrating moisture. However, because of plasticides and migration, sometimes the backing material separates from the adhesion. PVC backings are suitable for temperatures up to 60 °C (140 °F).

(2) Polyethylene tapes. Polyethylene-backed tapes most commonly are used with butyl or chlorinated rubber adhesives. These tapes are used as outer tapes to provide increased mechanical strength and UV light resistance. They can be used over primed steel as an inner tape wrap because of their excellent adhesive quality. Polyethylene tapes are considered suitable for use in cold climates because they retain their flexibility at temperatures as low as -40 °C (-40 °F). The polyethylene backing generally ranges from 0.25 to 1.27 mm (10 to 50 mils) thick; adhesive ranges from 0.08 to 0.30 mm (3 to 12 mils) thick.

(3) Petrolatum tapes.

(a) Petrolatum wax, obtained from the refining of petroleum, is purified and used as a corrosion-protective material. The petrolatum is a soft, viscous to semisolid waxy-like material with excellent wetting properties. Petrolatum tapes are fabricated by impregnating the petrolatum into a woven or nonwoven, cellulose-free synthetic fiber fabric, usually nylon or glass fiber. Inert fillers are added to improve thixotropy. The resulting coating possesses a low water vapor transmission rate, is relatively moisture impermeable, and is nondrying, nonhardening, nonhazardous, and nontoxic.

(b) Petrolatum tapes have some moisture-displacing capability and often are applied over hand- or power tool-cleaned surfaces (instead of blast-cleaned surfaces as required by most other tapes). Because of the high conformability of petrolatum tapes, they are suitable for use over irregular surfaces, on pipelines, and to protect valves, flanges, and other irregular shapes. Petrolatum tapes are soft and they are susceptible to mechanical damage. A polyvinyl chloride outer wrap or membrane is applied over the petrolatum tape to improve mechanical properties, particularly during handling and backfilling. This exterior wrap also keeps the petrolatum from oxidizing and drying out.

(c) Petrolatum formulations have been developed to allow use at temperatures as high as 82 °C (180 °F). These tapes are well suited for protecting metal couplings and valves and other pipeline irregularities and for coating repairs on existing pipes when the existing coating has deteriorated or failed in service.

(4) Coal-tar and asphalt tapes. Coal-tar and asphalt mastic tapes are used as hot-applied systems. The backing is usually a synthetic fiber of nylon or woven glass fiber. These tapes have good resistance to water penetration and, when properly applied, have excellent adhesion. They usually are used for over-the-ditch application and for the protection of welded joints.

(5) Butyl or EPDM vulcanized rubber tapes. Butyl or EPDM vulcanized rubber-backed tapes have excellent flexibility, mechanical resistance, and moisture resistance. The adhesive of these tapes is usually a butyl or chlorinated rubber, and this type of tape is noted for good adhesion and resistance to mechanical damage.

(6) Heat shrink polyolefin tapes. A crosslinked polyolefin backing is combined with a high shear strength crystalline adhesive to form a heat shrinkable pipeline tape. Prior to tape wrapping, the steel is usually hand- or power tool-cleaned and preheated to approximately 60 °C (140 °F). The tape is wrapped around a pipe with a 50 percent overlap and heated with a propane torch after wrapping. Heat from the torch causes the crystalline adhesive to melt and flow, filling surface irregularities. Additionally, the backing shrinks tightly to the steel substrate to provide good adhesion and conformability. There are calorimetric heating indicators in the backing to indicate when the proper temperature has been reached.

4-15. Other Coatings

Any listing of coating systems cannot be all-inclusive. There always will be specialized coating systems that are not widely used or are of little interest to USACE. Some of these systems may include fluoropolymer coating systems, used principally for high heat, corrosion-resistant surfaces; silicone resin coating systems, used as thin film, high heat systems or in combination with metal or ceramic frits for high heat, abrasion-resistant corrosion service; chlorinated rubber, neoprene, and other coating systems that are not widely manufactured and have been replaced by other generic-type coating systems; and variations or combinations of systems that are not different enough to warrant a separate category.