COATINGS FOR CORROSION CONTROL, ORGANIC

1. Introduction

Corrosion is a process by which materials, especially metals, are worn away by electrochemical and chemical actions. Metals have anodic and cathodic areas and in the presence of oxygen, water, and a conducting medium, corrosion results. The metal is oxidized to form metal ions at the anode and oxygen is reduced at the cathodes to form hydroxy ions. Since conductivity of the water is an important factor in the rate of corrosion, salts, such as sodium chloride, tend to increase the rate of corrosion.

The principal metals that corrode are steel and to a lesser extent aluminum. There are many kinds of steel; all are alloys of iron and carbon with other metals. Various kinds of steel corrode at different rates, depending on their composition and on the presence of mechanical stresses. The composition varies from location to location on the surface; as a result, some areas are anodic relative to other areas that are cathodic. Stresses and morphological structure of the metal surface can also be factors for setting up anode–cathode pairs. Cold-rolled steel has more internal stresses than hot-rolled steel and is generally more susceptible to corrosion; but, it is widely used because it is stronger. Internal stresses can also be created during fabrication or by the impact of a piece of gravel on an auto body.

Aluminum is higher in the electromotive series than iron and is more easily oxidized. Yet, aluminum generally corrodes more slowly than steel. A freshly exposed surface of aluminum oxidizes quickly to form a dense, coherent layer of aluminum oxide. On the other hand, aluminum corrodes more rapidly than iron under either highly acidic or highly basic conditions. Also, salt affects the corrosion of aluminum even more than it affects the corrosion of iron; aluminum corrodes rapidly in the presence of sea water.

Three strategies are employed to control electrochemical corrosion by coatings. First, one can cover the metal with a barrier coat to prevent water and oxygen from contacting the surface; second, one can suppress the anodic reaction, third, one can suppress the cathodic reaction.

In many cases, a metal object can be completely covered by intact coating films. However, there are situations where the metal surface cannot be

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completely covered or where an intact film is damaged during use. In such cases of nonintact films it is still essential to control corrosion.

2. Corrosion Protection by Intact Coatings

Coatings can be effective barriers to protect steel when it is anticipated that the coating can be applied to cover essentially all of the substrate surface and when the film remains intact in service. However, when it is anticipated that there will not be complete coverage of the substrate or that the film will be ruptured in service, alternative strategies using coatings that can suppress electrochemical reactions involved in corrosion may be preferable. It is seldom effective to try to use both strategies at the same time—one must choose one or the other.

2.1. Critical Factors. Until ~1950, coatings were generally believed to protect steel by acting as a barrier to keep water and oxygen away from the steel surface. Then it was found by Mayne (1) that the permeability of paint films was so high that the concentration of water and oxygen coming through the films would be higher than the rate of consumption of water and oxygen in the corrosion of uncoated steel. Mayne concluded that barrier action could not explain the effectiveness of coatings and proposed that the electrical conductivity of coating films is the variable that controls the degree of corrosion protection. Coatings with high conductivity would give poor protection, as compared to coatings of lower conductivity. It was confirmed experimentally that coatings having very high conductivity afforded poor corrosion protection. However, in comparisons of films with relatively low conductivity, little correlation between conductivity and protection has been found. It may be that high conductivity films fail because they also have high water permeability; some investigators believe that conductivity of all coatings is at least a factor in corrosion protection (2,3).

Current understanding of protection of steel against corrosion by intact films is based, to a significant degree, on the work of Funke (4–7). He found that an important factor not given sufficient emphasis in earlier work was adhesion of a coating to steel in the presence of water. Funke proposed that water permeating through an intact film could displace areas of film from steel. In such cases, the film shows poor *wet adhesion*. Water and oxygen dissolved in the water would then be in direct contact with the steel surface; hence, corrosion would start. As corrosion proceeds, ferrous and hydroxide ions are generated, leading to formation of an osmotic cell under the coating film. Osmotic pressure can provide a force to remove more coating from the substrate. Osmotic pressure can be expected to range between 2500 and 3000 kPa, whereas the resistance of organic coatings to deformational forces is lower, ranging from 6 to 40 kPa (4). Thus, blisters form and expand, exposing more unprotected steel surface. It has also been proposed that blisters can grow by a nonosmotic mechanism (8). The suggestion has been made that water absorbed by a coating induces in-plane compressive stress within the coating and elastically extends the interfacial bonds between the coating and the steel substrate (9). At a point of weak adhesion between the coating and the substrate, the stress can lead to disbondment. It has been demonstrated that the rate of growth of blisters is dependent on the modulus of the film, at a sufficiently high modulus blister growth is minimized (10).

In either osmotic or nonosmotic mechanisms, the key to maintaining corrosion protection by a coating is sufficient adhesion to resist displacement forces. Both mechanisms predict that if the coating covers the entire surface of the steel on a microscopic scale, as well as a macroscopic scale, and if perfect wet adhesion could be achieved at all areas of the interface, the coating would indefinitely protect steel against corrosion. It is difficult to achieve both of these requirements in applying coatings, so a high level of wet adhesion is important, but is not the only factor affecting corrosion protection by coatings. Funke found that in addition to wet adhesion, low water and oxygen permeability help increase corrosion protection (6). In any case, if wet adhesion is poor, corrosion protection is also poor. However, if the adhesion is fairly good, a low rate of water and oxygen permeation may delay loss of adhesion long enough so that there is adequate corrosion protection for many practical conditions.

Primers made with saponification resistant vehicles give better corrosion protection than primers made with vehicles that saponify readily (11,12). When water and oxygen permeate through a film and water displaces some of the adsorbed groups of the coating resin from the surface of the steel, corrosion starts. Hydroxide ions are generated at the cathodic areas. Hydroxide ions catalyze hydrolysis (saponification) of such groups as esters. If the backbone of the vehicle resin is connected by ester groups, hydrolysis results in polymer network degradation, leading to poorer wet adhesion and, ultimately, catastrophic failure.

2.2. Adhesion for Corrosion Protection.

Adhesion, especially wet adhesion, is critical to corrosion protection. Good dry adhesion is required; if there is no coating left on the substrate, it cannot protect the steel. It has not been so obvious, however, that good wet adhesion is required. Good wet adhesion means that the adsorbed layer of the coating will not desorb when water permeates through the film.

The first step to obtain good wet adhesion is to clean the steel surface, especially to remove any oils and salts. A monograph on methods for cleaning and treating metals for coating is available (13). Zinc and iron phosphate conversion coatings have been the standard treatment for many years. As the last step (often called sealing) before drying, the treated metal is rinsed with a chromic acid solution. Waste disposal problems are severe, especially considering the chromic acid wash step. Soluble chromium(VI) compounds have been shown to be carcinogenic and are being replaced as rapidly as possible. There are also reported to be toxic hazards associated with soluble nickel compounds.

It is reported that addition of polyethyleneimine to a Ca−Zn phosphating treatment bath gives a satisfactory conversion treatment without a chromate rinse (14). It has been shown that the chromate rinse step over zinc phosphate can be replaced with a rinse of a dilute solution of trimethoxymethylsilane with enough H_2ZrF_6 to bring the pH down to ~ 4 gave even better performance as a treatment for steel to be coated (15). Another patent covers treatment with a zinc/manganese phosphate solution containing silicotungstates followed by a hexafluorozirconic acid rinse (16). A patent has been applied for covering use of highly purified zinc nitrite as the accelerator with a zinc/manganese phosphate conversion coating in treating steel for electrodeposition (17). A nickel and chromium(VI)-free treatment system for steel and galvanized steel is carried out by washing with an alkaline cleaner, rinsing, treating with hexafluorozirconic acid, rinsing, and then sealing with a solution of epoxy phosphate (18). A combination of 3-aminopropyltriethoxysilane, a water-dispersible SiO_2, and zirconylammonium carbonate has been patented for surface treatment of steel and galvanized steel (19).

For many applications, aluminum does not have to be treated for corrosion control due to the coherent aluminum oxide surface of the aluminum. But if exposure to salt is to be expected, the surface must be treated before applying a coating. Chromate surface treatments have been the standard in the industry but with the concern about carcinogenicity of chromium(VI), proprietary chromium free treatments have been developed. Patents (or patent applications) have been issued covering chromium(VI)-free conversion treatments: chromium(III) sulfate plus potassium hexafluorozirconate (20), an aqueous solution of potassium manganate, potassium fluoride, potassium hydroxide, sodium hydrosulfite, and ortho-phosphoric acid (21), vanadium tetrafluoroborate among other similar compounds (22), and chromium(III) sulfate plus potassium hexafluorozirconate (23).

A patent application for treatment of cadmium and zinc–nickel coated steel with basic chromium(III) sulfate and potassium hexafluorozirconate and potassium hexafluorosilicate has been filed (24).

Bis(trialkoxysilyl)alkanes (BTSE) are being investigated to treat the surface of steel. Clean steel is treated with an aqueous solution of bis(triethoxysilyl)-ethane. The BTSE reacts with water and hydroxyl groups on the steel to give a water-resistant anchor on the steel. After drying, the treated metal can be coated and baked. For some types of coatings it is desirable to react the BTSE treated steel with a reactive silane that reacts with other silanol groups of the BTSE and provides a functional group to react with a coating binder (25). A patent has been issued disclosing such a process (26). Another patent covers the use of a combination of BTSE and a ureidotriethoxysilane to treat steel, galvanized steel, zinc, and aluminum (27). It is reported that galvanized steel treated with zirconium nitrate followed by treating with aminoethylaminopropyltrimethoxysilane and coated with a polyester primer gives equal performance to commercial chromate primed metal (28). A review of potential uses of silane treatments for steel, galvanized steel, and aluminum is available (29).

An investigation of the effect of treatment of the surface of galvanized steel with rare earth nitrates has been published (30). Lanthanum nitrate was particularly effective. The results are based on electrochemical testing of samples without organic coatings. Tests with organic coatings will be required before the utility of the treatment can be evaluated.

After cleaning and treating, the surface should not be touched and should be coated as soon as possible. Fingerprints leave oil and salt on the surface. After exposure to high humidity, fine blisters can form, disclosing the identity of the miscreant by the fingerprints. A rusty handprint was once observed on a ship after only one ocean and lake passage (3). When coating surfaces near the ocean, it is critical to avoid having any salt on the metal surface when the coating is applied.

It is also critical to achieve as nearly complete penetration into the micropores and irregularities in the surface of the steel as possible. If any steel is left uncoated, when water and oxygen reach the surface, corrosion will start, generating an osmotic cell that can lead to blistering. An important factor for achieving penetration is that the viscosity of the external phase of the coating be as low as possible and remain low long enough to permit complete penetration. It is desirable to use slow evaporating solvents, slow cross-linking coatings, and, when possible, baking primers. Macromolecules may be large compared to the size of small crevices, so lower molecular weight components may give better protection.

Wet adhesion requires that the coating not only be adsorbed strongly on the surface of the steel, but also that it not be desorbed by water that permeates through the coating. Empirically, it is found that wet adhesion is enhanced by having several adsorbing groups scattered along the resin chain, with parts of the resin backbone being flexible enough to permit relatively easy orientation and other parts rigid enough to assure that there are loops and tails sticking up from the surface for interaction with the rest of the coating. Another reason baking primers commonly provide superior corrosion protection is that at the higher temperature, there may be greater opportunity for orientation of resin molecules at the steel interface. Amine groups are particularly effective polar substituents for promoting wet adhesion. Perhaps, water is less likely to displace amines than other groups from the surface. Phosphate groups also promote wet adhesion. For example, epoxy phosphates have been used to enhance the adhesion of epoxy coatings on steel (31). Carboxylic acid-substituted polymers, such as polyacrylic acid, also promote wet adhesion by forming salt groups (32). However, if the coating is ruptured, the ready availability of water and the base generated by corrosion make polyacrylic acid ineffective. There is need for further research to understand the relationships between resin structure and wet adhesion.

Saponification resistance is another important factor. Corrosion generates hydroxide ions at the cathode, raising pH levels as high as 14. Ester groups in the backbone of a binder can be saponified, degrading the polymer near the interface and reducing wet adhesion. Epoxy-phenolic primers are an example of high bake primers that are completely resistant to hydrolysis. In some epoxy-amine primers, there are no hydrolyzable groups. Amine-terminated polyamides, which are widely used in air dry primers to react with epoxy resins, have amide groups in the backbone that can hydrolyze. However, amides are more resistant to base-catalyzed hydrolysis than are esters. Alkyd resins are used when only moderate corrosion protection is required and low cost is important. Epoxy ester primers show greater resistance to saponification than do alkyd primers.

Water-soluble components that stay in primer films should be avoided because they can lead to blister formation. For example, zinc oxide is an undesirable pigment to use in primers. Its surface interacts with water and carbon dioxide to form zinc hydroxide and zinc carbonate, which are somewhat soluble in water and can lead to osmotic blistering. Passivating pigments cannot function unless they are somewhat soluble in water; their presence in coating films can, therefore, lead to blistering. Funke showed that hydrophilic solvents, which become immiscible in the drying film as other solvents evaporate, can be retained as a separate phase and lead to blister formation (4).

2.3. Factors Affecting Oxygen and Water Permeability. Many factors affect permeability of coating films to water and oxygen (33). Water and oxygen can permeate, to at least some extent, through any amorphous polymer film, even though the film has no imperfections such as cracks or pores. Small molecules travel through the film by jumping from free volume hole to free volume hole. Free volume increases as temperature increases above glass-transition temperature T_g. Therefore, normally, one wants to design coatings with a T_g above the temperature at which corrosion protection is desired. Since cross-linking reactions become slow as the increasing T_g of the cross-linking polymer approaches the temperature at which the reaction occurs and become very slow at $T < T_g$, air dry films cannot have T_g values much above ambient temperatures. Water can act as a plasticizer for coatings such as epoxy-amines and polyurethanes; the swelling caused by the water increases internal stress that can lead to delamination (34). The internal stresses increase when a film is cycled through wet and dry stages. If the T_g is higher than the temperature of the water, water absorption is decreased, so internal stresses do not build up. The higher T_g values that can be reached with baked coatings may be another factor in their generally superior corrosion protection. In general, higher cross-link density leads to lower permeability. Both T_g and cross-link density affect other coating properties; so that some compromise between T_g and cross-link density and performance must be accepted.

Permeability is also affected by the solubility of oxygen and water in a film. The variation in oxygen solubility is probably small, but variation in water solubility can be large. Salt groups on a polymer lead to high solubility of water in films. This makes it difficult to formulate high-performance air dry, water-reducible coatings that are solubilized in water by amine salts of carboxylic acids. Although to a lesser degree than salts, resins made with polyethylene oxide backbones are likely to give high water permeabilities, as are silicone resins. On the other hand, water has low solubility in halogenated polymers; hence vinyl chloride and vinylidene chloride copolymers and chlorinated rubber are commonly used in formulating topcoats for corrosion resistance. Fluorinated polymers have low permeabilities and good wetting properties; hydroxy-functional poly(vinylidene fluoride) cross-linked with polyisocyanates is reported to give good corrosion protection even as a single coat (35).

Pigmentation can have significant effects on water and oxygen permeability. Oxygen and water molecules cannot pass through pigment particles; therefore, permeability decreases as pigment volume concentration (PVC) increases. However, if the PVC exceeds critical pigment volume concentration (CPVC), there are voids in the film, and passage of water and oxygen through the film is facilitated. Some pigments have high polarity surfaces that adsorb water, and in cases in which water can displace polymer adsorbed on such surfaces, water permeability can be expected to increase with increasing pigment content. Pigments should be used that are as free as possible of water-soluble impurities and use of hydrophilic pigment dispersants should be avoided, or at least minimized.

Pigments with platelet shaped particles can reduce permeability rates as much as fivefold when they are aligned parallel to the coating surface (5,36). A factor favoring alignment is shrinkage during solvent evaporation. Since oxygen and water vapor cannot pass through the pigment particles, the presence of aligned platelets can reduce the rate of vapor permeation through a film. The alignment is critical to the action of the platelets; if they are not aligned, permeability may be increased, especially if the film thickness is small relative to the size of the platelets. Mica, talc, micaceous iron oxide, glass flakes, and metal flakes are examples of such pigments. Aluminum flake is widely used; stainless steel and nickel platelets, while more expensive, have greater resistance to extremes of pH. When appearance permits, use of leafing aluminum pigment in the topcoat is particularly effective. Leafing aluminum is surface treated, so its surface free energy is very low. As a result, the platelets come to the surface during film formation, creating an almost continuous barrier. In formulating coatings with leafing aluminum, it is necessary to avoid resins and solvents that displace the surface treatment from the flakes.

A Monte Carlo simulation model of the effect of several variables on diffusion through pigmented coatings has been devised (37). The model indicates, as would be expected, that finely dispersed, lamellar pigment particles at a concentration near, but below CPVC, give the best barrier performance.

There are advantages to applying multiple layers of coatings. The primer can be designed so that it has excellent penetration into the substrate surface, has excellent wet adhesion, and saponification resistance without particular concern about other properties. The topcoat(s) can provide for minimum permeability and other required properties. The primer film does not need to be thick, as long as the topcoat is providing barrier properties; the lower limit is probably controlled by the need to assure coverage of the entire surface. Funke has reported good results with 0.2-μm primer thickness (7), or even a 10 nm layer of a wet adhesion promoting polymer (32). Another advantage of applying multiple coats is the decrease in probability that any area of the substrate will escape having any coating applied.

Film thickness affects the time necessary for permeation through films. Thicker films are expected to delay somewhat the arrival of water and oxygen at the interface, but are not expected to affect the equilibrium condition. The corrosion protection afforded by intact films would be expected to be essentially independent of film thickness. However, since film thickness affects the mechanical performance of films, there may be some optimum film thickness for the maintenance of an intact film. For example, erosion losses would take longer to expose bare metal as film thickness increases, but the probability of cracking on bending increases as film thickness increases. However, in air dry, heavy duty maintenance coatings, there is generally a film thickness, dependent on the coating that provides a more than proportional increase in corrosion protection relative to thinner films. Commonly, this film thickness is as much as 400 μm or more. Below certain coating thicknesses, there may be microscopic defects extending down through the film to the substrate. The film may look intact, but there may be microscopic defects that are large compared to the free volume holes through which permeation in fully intact films occurs. A potential source of such defects is cracks resulting from shrinkage of films as the last solvent is lost from a coating, with the T_g of the solvent-free system around ambient temperature. If the film is thick enough, such defects may not reach the substrate, hence substantially reducing passage of water and oxygen. This hypothesis is consistent with the general observation that greater protection is achieved by applying more coats to reach the same film thickness. In line with this proposal, the use of barrier platelet pigments permits a reduction in the required film thickness without loss of protection. The platelets may minimize the probability of defects propagating through the film to the substrate. Such defects are less likely to occur in baked films, and this may be another factor in the generally superior corrosion protection afforded by baked films, even though thinner film thicknesses are used.

3. Corrosion Protection by Nonintact Films

Even with coatings designed to minimize the probability of mechanical failure, in many end uses, there will be breaks in the films during their service life. There are situations in which it is not possible to have full coverage of all the steel surface. In such cases, it is generally desirable to design coatings to suppress electrochemical reactions, rather than primarily for their barrier properties.

3.1. Minimizing Growth of Imperfections. If there are gouges through the film down to bare metal, water and oxygen reach the metal and corrosion starts. If the wet adhesion of the primer to the metal is not adequate, water creeps under the coating, and the coating comes loose from the metal over a wider and wider area. Poor hydrolytic stability can be expected to exacerbate the situation. This mode of failure is called cathodic delamination. Control of cathodic delamination requires wet adhesion and saponification resistance. It has also been shown that blisters are likely to develop under a film near the location of a gouge (5,38).

When wet adhesion varies on a local scale, *filiform corrosion* can occur (39). It is characterized by development of thin threads of corrosion wandering randomly under the film, but never crossing another track. Formation of these threads often starts from the edge of a scratch. At the head of the thread, oxygen permeates through the film, and cathodic delamination occurs. The head grows following the directions of poorest wet adhesion. Behind the head, oxygen is consumed by oxidation of ferrous ions and ferric hydroxide precipitates, passivating the area, explaining why threads never cross. Since the ion concentration decreases, osmotic pressure drops, and the thread collapses, but it leaves a discernable rust track. Filiform corrosion can be difficult to see through pigmented films. Infrared (ir) thermography may be a useful way of detecting filiform corrosion of such films (40).

3.2. Passivating Primers. There are inhibitors that suppress corrosion. An important class acts by retarding the anodic reaction, they are called *passivators*. A passivator suppresses corrosion above some critical concentration, but may accelerate corrosion at lower concentrations by cathodic depolarization. This phenomenon is illustrated by the effect of oxygen concentration on corrosion rate. Increasing oxygen concentration up to $\sim$12 mL/L increases corrosion rate because it acts to depolarize the cathode. That is, it oxidizes the hydrogen released at the cathode by electrolysis of water. At higher concentrations, more oxygen reaches the surface than is reduced by the cathodic reaction; beyond that concentration, oxygen is a passivating agent. The mechanism of passivation has not been fully elucidated. According to one theory, if the oxygen concentration near the anode is high enough, ferrous ions are oxidized to ferric ions soon after they are formed at the anodic surfaces. Since ferric hydroxide is less soluble in water than ferrous hydroxide, a barrier of hydrated ferric oxide forms over the anodic areas. The iron is said to be passivated.

Passivating pigments promote formation of a barrier layer over anodic areas, passivating the surface. To be effective, such pigments must have some minimum solubility. However, if the solubility is too high, the pigment would leach out of the coating film too rapidly, limiting the time that it is available to inhibit corrosion. For the pigment to be effective, the binder must permit diffusion of water to dissolve the pigment. Therefore, the use of passivating pigments may lead to blistering after exposure to humid conditions. Such pigments are most useful in applications in which the need to protect the steel substrate after film rupture has occurred outweighs the desirability of minimizing the probability of blistering. They are also useful when it is not possible to remove all surface contamination (blistering will probably occur anyway) or when it is not possible to achieve complete coverage of the steel by the coating.

The critical oxygen concentration for passivation depends on conditions. It increases with dissolved salt concentration and with temperature, and it decreases with increases in pH and velocity of water flow over the surface. At ~pH 10, the critical oxygen concentration reaches the value for air-saturated water (6 mL/L) and is still lower at higher pHs. As a result, iron is passivated against corrosion by the oxygen in air at sufficiently high pH values. It is impractical to control corrosion by oxygen passivation below ~pH 10, since the concentrations needed are in excess of those dissolved in water in equilibrium with air. However, a variety of oxidizing agents can act as passivators. Chromate, nitrite, molybdate, plumbate, and tungstate salts are examples. As with oxygen, a critical concentration of these oxidizing agents is needed to achieve passivation. The reactions with chromate salts have been most extensively studied. Partially hydrated mixed ferric and chromic oxides are deposited on the surface, where they presumably act as a barrier to halt the anodic reaction.

Certain nonoxidizing salts, such as alkali metal salts of boric, carbonic, phosphoric, and benzoic acids, also act as passivating agents. Their passivating action may result from their basicity. By increasing pH, they may reduce the critical oxygen concentration for passivation below the level reached in equilibrium with air. Alternatively, it has been suggested that the anions of these salts may combine with ferrous or ferric ions to precipitate complex salts to form a barrier coating at the anode. There is a possibility that both mechanisms may operate to some extent.

A fairly new approach to passivation is applying a film of electrically conductive polymer to a steel surface to protect it from corrosion. Polyphenyleneamine, commonly called polyaniline, is available commercially under the trade names Zypan (41) (DuPont), Versicon (Allied Signal Co.), and Panda (Monsanto Co.). It is said to be effective by leading to the formation of tight, very thin, metal oxide passivating layer on the surface of the metal. The polymer powders are insoluble in all solvents, nonfusible, and difficult to disperse because of high surface tension. Dispersions in a variety of vehicles are available. Reviews of the effects of conducting polymer coatings on metals are available (42,43). Another review of conducting polymer coatings emphasizes protection of aluminum with poly[2,5-bis(*N*-methyl-*N*-propylamino)phenylenevinylene] (44).

Many organic compounds are corrosion inhibitors for steel. Most are polar substances that tend to adsorb on high energy surfaces (38). Amines are particularly widely used. Clean steel wrapped in paper impregnated with a volatile amine or the amine salt of a weak acid is protected against corrosion. The reason for their effectiveness is not clear. They may act as inhibitors because they are bases and neutralize acids. It may be that amines are strongly adsorbed on the surface of the steel by hydrogen bonding or salt formation with acidic sites on the surface of the steel. This adsorbed layer then may act as a barrier to prevent oxygen and water from reaching the surface of the steel.

To protect uncoated steel and aluminum components during shipment and storage, strippable coatings can be used. For example, a coating comprised of two aqueous polyurethane dispersions with aminomethylpropanol is sprayed over the surfaces as a protective layer (45). The coating is easily removed and can be recycled.

Red lead pigment, Pb_3O_4 containing 2–15% PbO, has been used as a passivating pigment since the mid-nineteenth century. Red lead-in-oil primers are used for air dry application over rusty, oily steel. The mechanisms of action are not fully understood (38). They presumably include oxidation of ferrous ions to ferric ions followed by coprecipitation of mixed iron–lead salts or oxides. The somewhat soluble PbO raises the pH and neutralizes any fatty acids formed over time by hydrolysis of the drying oil. Toxic hazards of red lead restrict its use to certain industrial and special purpose applications, and regulations can be expected to prohibit its use.

The utility of chromate pigments for passivation is well established. Various mechanisms have been proposed to explain their effectiveness (38). All the proposed mechanisms require that the chromate ions be in aqueous solution. Like all passivators, chromate ions accelerate corrosion at low concentrations. The critical minimum concentration for passivation at 25°C is $\sim 10^{-3}$ mol CrO_4^{2-}/L. The critical concentration increases with increasing temperature and increasing NaCl concentration. Sodium dichromate is an effective passivating agent, but would be a poor passivating pigment; its solubility in water (3.3 mol CrO_4^{2-}/L) is too high. It would be rapidly leached out of a film and would probably cause massive blistering. At the other extreme, lead chromate (chrome yellow) is so insoluble (5×10^{-7} mol CrO_4^{2-}/L) that it has no electrochemical action.

"Zinc chromates" have been widely used as passivating pigments. The terminology is poor, since zinc chromate itself is too insoluble and could promote corrosion, rather than passivate. Zinc yellow pigment is [$K_2CrO_4 \cdot 3Zn$-$3ZnCrO_4 \cdot Zn(OH)_2 \cdot 2H_2O$]. Zinc tetroxychromate [$ZnCrO_4 \cdot 4Zn(OH)_2$] has a solubility lower than desirable (2×10^{-4} mol CrO_4^{2-}/L), but is used in *wash primers*. Phosphoric acid is added to wash primers before application; it may be that this changes the solubility so that the chromate ion concentration is raised to an appropriate level. Strontium chromate ($SrCrO_4$) has an appropriate solubility in water (5×10^{-3} mol CrO_4^{2-}/L) and is sometimes used in primers, especially latex paint primers, in which the more soluble zinc yellow can cause problems of package stability.

It has been established that zinc chromates—and, presumably, other soluble chromates—are carcinogenic to humans. They must, therefore, be handled with appropriate caution. In some countries, their use has been prohibited; their use has been prohibited in Los Angeles and it is expected that this will be expanded statewide in California. Prohibition worldwide is probable in the future.

Substantial efforts have been undertaken to develop less hazardous passivating pigments (46). However, it is difficult to conclude from the available literature and supplier technical bulletins on how these pigments compare with each other and with zinc yellow. In some cases, a formulation that has been optimized for one pigment is compared to a formulation containing another pigment that may not be the optimum formulation for that pigment. (A common example is the substitution of one pigment for another on an equal weight basis, rather than formulating to the same ratio of PVC to CPVC; the results could be very misleading, since primer performance is quite sensitive to the PVC/CPVC ratio.) Much of the published data is based on comparing corrosion resistance in salt fog chamber tests (or other laboratory tests) rather than on actual field experience. A problem with accelerated tests is that an important factor in the performance of a pigment is the rate at which it is leached from a film. A pigment could be sufficiently insoluble that it is not fully dissolved in 1000–2000 h in an accelerated test but be fully dissolved in field applications where corrosion protection for several years is required. As discussed later, there is no laboratory test available that provides reliable predictions of field performance.

Basic zinc and zinc–calcium molybdates are said to act as passivating agents in the presence of oxygen, apparently leading to precipitation of a ferric molybdic oxide barrier layer on the anodic areas. Barium metaborate is the salt of a strong base and a weak acid. It may act by increasing the pH, thus lowering the critical concentration of oxygen required for passivation. To reduce its solubility in water, the pigment grade is coated with silicon dioxide. Even then, some workers feel that the solubility is too high for use in long-term exposure conditions. Zinc phosphate, $Zn_3(PO_4)_2 \cdot 2H_2O$, has been used in corrosion protective primers and may act by forming barrier precipitates on the anodic areas. There is a considerable difference of opinion as to its effectiveness. Calcium and barium phosphosilicates and borosilicates are being used increasingly; they may act by increasing pH. Calcium tripolyphosphate has also been recommended (47).

These pigments are all inorganic pigments; a wider range of potential oxidizing agents would seem to be available if organic pigments were used. An example of a commercially available organic pigment is the zinc salt of 5-nitroisophthalic acid. It is said to be as effective as zinc yellow at lower pigment levels. (Since over a long time, any effective passivating pigment will be lost by leaching, it seems doubtful that an equal lifetime could be achieved at a substantially lower pigment content.) The zinc salt of 2-benzothiazoylthiosuccinic acid has been recommended as a passivating agent.

Reference 48 reviews the subject of passivating pigments and reports that hybrid inorganic/organic pigments can equal the performance of strontium chromate. A patent discloses manufacture procedures for inorganic/organic anticorrosion pigments such as $Zn(NCN)_2$/Zn(2-mercaptobenzothiazole) (49).

3.3. Cathodic Protection by Zinc-Rich Primers. *Zinc-rich primers* are another approach to protecting steel with nonintact coatings. They are designed to provide the protection given by galvanized steel, but to be applied to a steel structure after fabrication (50). The primers contain high levels of powdered zinc, $>80\%$ by weight is usual. On a volume basis, the zinc content exceeds CPVC to assure good electrical contact between the zinc particles and with the steel. Furthermore, when PVC is $>$CPVC, the film is porous, permitting water to enter, completing the electrical circuit. The CPVCs of zinc powders vary, depending primarily on particle size and particle size distribution; values on the order of 67% have been reported (51). The zinc serves as a sacrificial anode, and zinc hydroxide is generated in the pores. Since corrosion protection with zinc-rich primers, depends on maintaining the open pore structure of the primer so as to maintain electrical conductivity, topcoats must not penetrate significantly into the primer.

Vehicles for zinc-rich primers must be saponification resistant. Two classes of binders are used, organic resins and inorganic resins. Alkyds are not appropriate resins for this application since they are readily saponified. Two package (2K) epoxy/amine systems are commonly used. Zinc-rich primers with moisture-cure urethanes are used for new construction when the metal surface is blast cleaned to white metal conditions (52). Reference (53) provides a discussion of variables in formulating such zinc-rich primers. Urethane coatings have adequate saponification resistance and have the advantage over epoxy/amine coatings of being one package coatings. Water-borne urethane coatings are also available. For example, a zinc-rich primer is formulated with an aqueous polyurethane dispersion (PUD) made from a polyether diol, *N*-(3-trimethoxysilylpropyl)aspartic acid diethyl ester, and bis(4-isocyanatophenyl)methane diisocyanate (54).

However, the most widely used vehicles are tetraethyl orthosilicate and oligomers derived from it by controlled partial hydrolysis with a small amount of water. Ethyl or isopropyl alcohol is used as the principal solvent, since an alcohol helps maintain package stability. After application, the alcohol evaporates, and water from the air completes the hydrolysis of the oligomer to yield a film of polysilicic acid partially converted to zinc salts. Cross-linking is affected by relative humidity (RH); properties can be adversely affected if the RH is low at the time of application. Such a primer is referred to as an *inorganic zinc-rich primer*. The need to reduce VOC emissions has led to the development of water-borne zinc-rich primers. These use sodium, potassium, and/or lithium silicate solutions in water as the vehicle. In many applications, they have been found to be as useful as solvent-borne zinc-rich primers. However, they have limitations: sensitivity to high humidity, slow rate of evaporation, relatively poor wetting and flow. Properties are effected by the ratio of the silicate to alkali and particle size and distribution of the zinc dust (55). The chemistry of silicate binders is reviewed in (56).

Properly formulated and applied, zinc-rich primers are very effective in protecting steel against corrosion. Their useful lifetime is not completely limited by the amount of zinc present, as one might first assume. Initially, the amount of free zinc decreases from the electrochemical reaction; later, loss of zinc metal becomes slow, but the primer continues to protect the steel. Possibly, the partially hydrated zinc oxide formed in the initial stages of corrosion of the zinc fills the pores and, together with the remaining zinc, acts as a barrier coating

(57). It is also possible that the zinc hydroxide raises the pH to the level at which oxygen can passivate the steel.

Zinc is expensive, especially on a volume basis. Early attempts to replace even 10% of the zinc with low-cost inert pigment caused a serious decrease in performance, presumably due to decrease in metal to metal contact, even though the PVC was >CPVC. A relatively conductive inert pigment, iron phosphide (Fe_2P), has shown promise (58). It has been reported that in ethyl silicate-based coatings, up to 25% of the zinc can be replaced with Fe_2P; however, with epoxy-polyamide coatings replacement of part of the Zn with Fe_2P leads to a reduction in protection (59).

Zinc-rich powder coatings cannot be applied with the PVC above CPVC. Lower zinc content powder coatings have been used but corrosion protection is inferior to liquid applied coatings because of low penetration of water through the coating and inferior contact between zinc particles and between them and the steel substrate. It has been found that addition of sufficient carbon black increases electrical conductivity between zinc particles and with the substrate providing good performance (60).

Zinc-rich primers are frequently topcoated to minimize corrosion of the zinc, protect against physical damage, and improve appearance. Formulation and application of topcoats must be done with care. If the vehicle of the topcoat penetrates into the pores in the primer film, conductivity of the primer may be substantially reduced, rendering it ineffective.

4. Types of Coatings

4.1. Primers for Baked Coatings.

In most cases, baking primers are designed to be barrier coatings to minimize the risk of blistering. Primers formulated with epoxy and phenolic resins provide excellent corrosion over steel; they show good wet adhesion and are not subject to hydrolysis or saponification. Epoxy ester based primers cure at a somewhat lower temperature and approach epoxy-phenolic coatings in performance. Polyurethane primers can provide good properties. To minimize cost they are prepared with aromatic polyisocyanates but even then their cost tends to be higher than epoxy/amine primers. Alkyd resins are only used when performance requirements are limited. They have the advantage of low cost and ease of application but are subject to saponification.

Primers are generally formulated with PVC only slightly under CPVC. There are two resins for the high pigment loading. The pigment minimizes water and oxygen permeability especially if part of the pigment is a platy pigment such as mica or micaceous iron oxide. Also, the low gloss surface of a highly pigmented primer decreases the difficulty of having good intercoat adhesion with the topcoat. The high pigmentation of primers makes formulation of very high solids primers impossible. The upper limit of solids is ~70 vol%. As a result, the incentive to develop water-borne primers is high.

The most widely used water-borne primers are formulated with maleinized epoxy esters; most commonly dehydrated castor oil based epoxy esters. An epoxy ester is reacted with maleic anhydride (2,5-furandione) [108-31-6] that undergoes a Diels-Alder reaction with the conjugated double bonds of the dehydrated castor oil fatty acids. In this way, the acid groups are attached to the resin by carbon-to-carbon bonds and cannot be removed by hydrolysis. The maleated resin is reacted with an amine such as dimethylethanolamine and dispersed in water. Performance of primers based on this vehicle is fully comparable to that of solvent-borne epoxy ester primers.

Coil coating is sometimes an exception to the general statement that barrier coatings are used for corrosion protection with baked coatings. When coil coated steel is fabricated there are cut edges exposed. Corrosion can start at these cut edges. Epoxy ester primers with a chromate passivating pigment have been used. In a study of the effect of passivating pigment on cut edge corrosion of coil coated galvanized steel with a polyester/melamine–formaldehyde primer, it has been reported that $AlH_2P_3O_{10} \cdot 2H_2O$ (K White 84) and a proprietary pigment (Actinox-106) containing both PO_4 and MoO_3 anions provided protection close to that of strontium chromate (61).

4.2. Electrodeposition Coatings. Cationic electrodeposition coatings are used as primers on all automobiles and trucks as well as many other steel substrates. Reference (62) is an old but still useful review of cationic E-coats. A more recent review of electrodeposition coatings is given in (63).

The article to be coated is submerged on a conveyor in a tank and made the cathode of a electrolytic cell. The coating is an aqueous dispersion of a cationic resin system. The dispersed particles are electrophoretically attracted by the cathode at which OH^- ions are being generated by the electrolysis of water. The charges on the coating particles are neutralized leading to the deposition of a layer of coating on the cathode. It is critical that the binder be very resistant to hydrolysis or saponification.

The coatings must be designed so that all components are in the aggregate particles so that all components in composition are attracted to the electrode at the same rate. The electrolysis of water leads to the release of the neutralizing acid at the anode, which must be removed. The rate of deposition and deposition in restricted areas is affected by the conductivity of the aqueous phase. As the coated object on the conveyor moves out of the tank it must be rinsed so that the system is being continually being diluted. The dilution effect and the accumulation of acid can be partially made up for by adding new primer at higher solids and with a deficiency of acid. But also, an ultrafilter is required to remove excess water, soluble salts, and excess acid.

The rate of deposition increases with increasing voltage. As film thickness increases the rate of deposition decreases and finally stops as the electrical resistance increases. If the voltage is too high, hydrogen gas evolved below the surface of the coating erupts through the coating. If the conductivity of the aqueous phase is too high, the rate of deposition will decrease. The balance of conductivity and voltage is critical in controlling “throw power,” that is the distance of deposition into a closed end narrow hollow in the object.

The coating composition consists of an amine modified 4,4′-(1-methylethylidene)bisphenol (BPA) [80-05-7] epoxy resin such as shown in Figure 1 with a blocked polyisocyanate as the cross-linker.

For many years, the blocking agent for the polyisocyanate was 2-ethylhexyl alcohol (2EH). Since 2EH blocked isocyanates have to be heated to temperatures in the range of 180°C for 30 min to cure, there has been a major amount of work

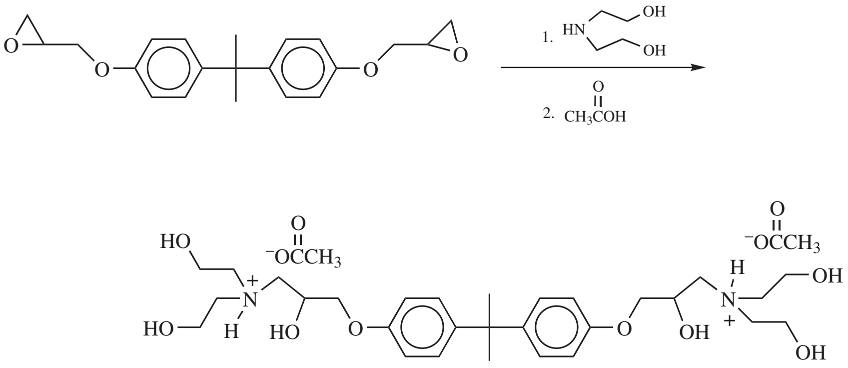

Fig. 1. Formation of water-dispersible BPA epoxy adduct.

devoted to studying other blocking agents. Butoxyethoxyethanol is an example of a blocking agent that permits cure at 150°C. See (64) for an extensive review of blocked isocyanates for E-coat.

The cross-linker for almost all E-coats is a blocked isocyanate usually derived from toluene diisocyanate (TDI), (2,4-diisocyanato-1-methylbenzene) [584-84-9], or bis(4-isocyanatophenyl)methane (MDI). Commonly, a half-blocked isocyanate such as shown in Figure 2 is reacted with the epoxy−amine compound before neutralization with acetic acid (or other low molecular weight carboxylic acid). Pigments are dispersed in the vehicle and the pigmented coating is dispersed in water.

There has also been substantial effort to find more effective catalysts for the cross-linking reaction. In early primers, it was common to use a combination of dibutyltin oxide and basic lead silicate or lead cyanamide as the catalyst. To remove the lead and lower cure temperatures many alternative catalysts have been patented (64). It is essential that a catalyst be very resistant to hydrolysis, eg, dibutyltin dilaurate dibutyl bis[1-(oxododecyl)oxy]-stannate (DBTDL) [77-58-7] is too easily hydrolyzed. Bis(trioctyltin) oxide is one example of a

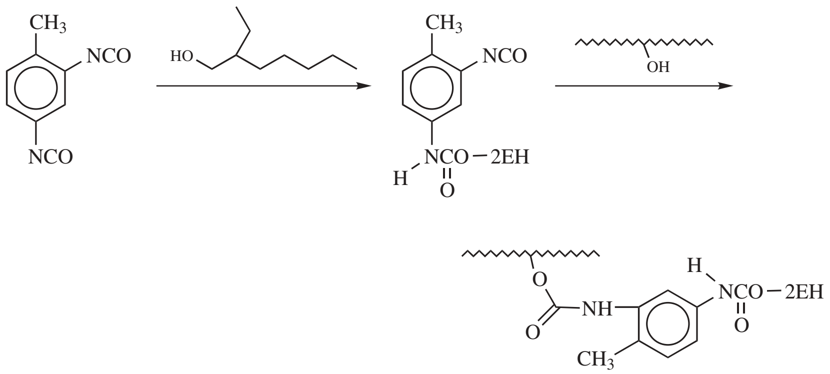

Fig. 2. Formation of half-blocked TDI-2EH adduct.

catalyst whose use in E-coats has been patented (65). See (64) for a review of catalysts for E-coating.

A patent has been applied for disclosing use of a carbamate-functional resin prepared by reacting a BPA epoxy resin with isophorone diisocyanate [1-isocyanato-3-(isocyanatomethyl)-3,5,5-trimethylcyclohexane] [4098-71-9] that has been partially reacted with hydroxypropylcarbamate. The resin is then reacted with dimethylethanolamine and formic acid to provide for water dispersibility. The cationic E-coat composition is formulated with this resin and butylated MF resin as the cross-linker. The coating has the advantage of curing in 30 min at a metal temperature of 100°C while retaining the property advantages resulting from the presence of carbamate (urethane) groups (66).

The corrosion resistance of automobiles coated by cationic E-coating is excellent. This results because of the strong interaction between the amine groups on the coating and the steel and its phosphate coating leads to excellent wet adhesion. Also, the film completely covers the surface and penetrates into all the micropores on the surface by the driving force of the electrocoating and the high temperature baking. The urethane cross-linked epoxy resin is almost impervious to saponification.

The film thickness applied is uniform, which means that any irregularities in the surface of the metal are copied in the surface of the primer coat. Also, since the pigmentation must be lower than usual in primers, adhesion to the surface of topcoats can be difficult to achieve. In general, a coat of a primer-surfacer is applied over the primer before topcoating. Another approach is to apply two E-coats, the first designed to provide the excellent wet adhesion to the steel, and the second one that is designed to provide a level surface to which topcoats will adhere. One example of a patent covering a conductive E-coat primer discloses a formulation using 2EH blocked TDI with an epoxy-amine resin and electroconductive black pigment (67).

4.3. Maintenance Paints. Maintenance paints are coatings applied to field installations such as highway bridges, factories, and tank farms. Composition of the coating is a main variable but surface preparation and application procedures are also critical to performance. The most commonly used method of cleaning has been sandblasting, however, conventional sand blasting is being rapidly replaced by modifications that are less hazardous. Abrasive blasting with materials like steel grit or water-soluble abrasives like sodium bicarbonate or salt are replacing sand that can cause silicosis. Ultra-high pressure hydroblasting at pressures >175 mPa (25,000 psi) is very effective in removing oil and surface contaminants such as salt. Salt on the surface of steel to be painted is a major source of failure by osmotic blistering. Reference (68) reviews methods of testing the surfaces for salt content and effects on corrosion. Only a limited area should be cleaned at a time so that coating can be applied before contamination. A patent has been issued covering the replacement of grit blasting with a phosphoric acid wash, rinse, phosphate conversion treatment, rinse and a chrome-free sealer (69).

At least two coats, primer and topcoat, are applied; in some cases a primer, intermediate coat, and a topcoat are required. The primer provides the principal protection against corrosion but the other coats also help reduce water and oxygen permeability as well as protecting the primer and providing the desired surface properties. Three types of primers are used depending on the applications: barrier primers, zinc-rich primers, and primers containing passivating pigments.

Barrier Coating Systems. The primer must have excellent wet adhesion. It should have a low viscosity and slow evaporating solvents to permit penetration into microcracks and crevices in the steel surface. Amine and phosphate groups tend to promote wet adhesion. The T_g of the fully cured film should be only a little above the ambient temperature at which the film will be cured. If the T_g of the fully cross-linked film is significantly above ambient temperature, cure rate will slow and may well stop before full cure is attained.

Two package (2K) primers formulated with BPA or novolak epoxy resins and polyfunctional amines are widely used. They can provide excellent wet adhesion and do not saponify. To reduce VOC emissions, water-borne 2K epoxy/amine coatings have been developed whose properties approach those of solvent borne primers (70). Epoxy/amine primers have poor exterior durability and must be topcoated. Chlorinated rubber or vinyl chloride copolymers are desirable in topcoats because of their low permeability to water, however, VOC emissions are high.

Moisture-cure urethane primers can be used over old lead containing coatings reducing the hazards resulting from removal of the old coating. In contrast to many other types of finishes, good protection can be achieved by hand tool cleaning. Such cleaning removes loose old paint but the cleaning still leaves areas of adherent rust and grease, for good performance the viscosity of the external phase of a primer should be very low to permit penetration into the rust areas and crevices in the steel. Such primers are sometimes called sealers (71). A proprietary TDI/polyol prepolymer is reported to have much narrower molecular weight distribution than a conventional TDI/polyol prepolymer (72). Consequently, it has a lower viscosity, hence permitting higher solids primers to be formulated. The corrosion protection is also reported to be superior to that obtained using a conventional primer. A further advantage for moisture-cure urethanes for this application is that they react with water that usually is in and under the rust areas. The coatings are 1K in contrast to 2K epoxy primers that have been used. There are also the advantages that that they can be applied at low temperatures and relatively high humidity.

Micaceous iron oxide pigmented moisture-cure urethane primers have been recommended for application to steel surfaces requiring exposure to weather with air-borne pollution (73). They have outstanding chemical and abrasion resistance. They can be applied under cold, damp conditions. They are said to have good adhesion to damp surfaces. The coatings are not washed away by rain. Reference (74) provides a useful discussion of moisture-curing urethane coatings for maintenance coatings.

2K urethane primers are being successfully used, usually with 2K urethane topcoats. High solids coatings ($>70\%$ solids) are available. The 2K water-borne urethane coatings are now available and used on a wide scale. Reference (75) is a recent review of the field. A review of 2K water-borne urethane maintenance coatings has been published (76). Use of a proprietary water-reducible acrylic resin with conventional HDI based isocyanates is particularly recommended.

Since zinc rapidly develops strongly basic corrosion products, vehicles for primers galvanized steel must be very resistant to saponification. An extensive study of coatings on galvanized steel at Cape Kennedy, Florida for 4.5 years showed that the best performance with an epoxy–polyamide primer and a urethane topcoat (77).

Zinc-Rich Primers. Zinc-rich primers can provide excellent performance when a surface cannot be completely cleaned of rust or when, as is the case with latex coatings, complete penetration into surface pores cannot be achieved. There are three classes of zinc-rich primers: inorganic, organic, and water-borne, In the inorganic primers, the vehicle is partially hydrolyzed tetraethyl orthosilicate in an alcohol solvent. After application the solvent evaporates and reaction with water completes the polymerization. Cross-linking is affected by humidity. Organic primers are made with epoxy resins vehicles. They are in general not as effective as inorganic primers but have greater tolerance for incomplete removal of oils from the surface and better compatibility with topcoats. Water-borne primers are made with a vehicle of potassium, sodium, and/or lithium silicates with a dispersion of colloidal silica. Excellent performance on oil and gas production facilities in marine environments has been reported (78).

A challenge in the use of zinc-rich primers is the proper selection and application of topcoats. Activity of the primer depends on maintaining the porous structure that results from having the PVC > CPVC. If a topcoat penetrates into the pores, the required conductive contacts between zinc particles will be interrupted. Penetration can be minimized by spraying a very thin coat uniformly on the surface, in this way the solvent evaporates rapidly, hence the viscosity increases rapidly to minimize penetration. Applying such a coating uniformly requires a very skillful sprayer. After this first coat is applied, further topcoat can be applied without difficulty. Since latex paints have no resin in the continuous phase, there is less difficulty in applying them over zinc-rich primers. In California, extensive tests have shown that zinc-rich primers with a latex paint topcoat gave excellent protection of highway bridges. It was recommended that application should only be done when the temperature is >10°C and the relative humidity is <75%. Latex paints in general have high moisture permeabilities so it is particularly desirable to formulate with platy pigments. Vinylidene chloride/acrylic latexes have lower moisture permeability and have been used (79).

Passivating Primers. When film damage must be anticipated and when the substrate cannot be completely cleaned, primers with passivating pigments may be the primers of choice. Zinc yellow pigment was for many years the pigment of choice, but it is now known that it is a carcinogen. Since there is no way to evaluate the performance of new pigments in a laboratory, it has been difficult to establish satisfactory replacements. Basic zinc and zinc-calcium molybdates, calcium and barium phosphosilicates and borosilicates, and zinc 5-nitroisophthalate are examples of current pigments. The vehicles for these primers are epoxy-amines, epoxy esters, and urethanes.

In a study of chromium-free passivating pigments in water-borne epoxy/amine coatings, zinc iron phosphate, zinc aluminum phosphate, and zinc molybdenum phosphate were given the highest ratings (80).

Use of latex paints over sand blasted steel leads to “flash rusting.” That is, there is virtually instantaneous rusting across the surface when the paint is applied. Commonly, 2-amino-2-methyl-propan-1-ol is added to a latex paint to eliminate the problem. Use of mercaptan substituted compounds as additives to prevent flash rusting has also been recommended (81).

A fairly new approach to achieving passivation is to apply a thin coat of an electrically conducting polymer to steel. A thin, dense layer of iron oxide forms on the steel surface that acts as a passivating layer. Perhaps the effect is enhanced by a strong attraction between amine groups on the polymer with the oxide layer. The corrosion resistance with various topcoats over polyaniline (Panda) films on cleaned steel has been reported (42). Excellent resistance to salt spray tests was obtained. A patent discloses the uses of a variety of dispersions of polyaniline with a variety of organic coatings (82). Another patent discloses 2K coatings formulated with one package containing a polyamide resin, polyaniline powder, and aluminum powder, the other with a BPA epoxy resin (83). In another patent, polyaniline coated nylon 12 polymer particles are dispersed in an epoxy ester resin (84).

4.4. Automotive Refinishing. When major damage has been experienced on a component, such as a door, it is common practice to use a replacement component that has been E-coated by the car manufacturer. Unfortunately, there are uncertified components that have only a black lacquer film on them, this should be removed. When bare metal has to be refinished wash primers are most often used. The binders of wash primers are poly(vinyl butyral) and a phenolic resin, they are generally pigmented with zinc tetroxychromate. Acid is added just before application and a wash coat (very thin coating) is applied to the bare metal. Wash primers give excellent adhesion for topcoats and provide excellent corrosion resistance. Such primers have very high VOC emissions but, except in California, their use has been allowed. Unpigmented wash primers have also been developed that offer properties very close to those with chromium.

4.5. Aircraft Coatings. Primers for exterior surfaces are 2K BPA epoxy/amino-amide-based coatings with a passivating pigment. Strontium chromate has been the pigment of choice. Interior components such as baggage areas are coated with a novolak epoxy amine coating pigmented with strontium chromate and generally not topcoated. Increasingly, water-borne epoxy primers are being used (85). 2K systems in which the amine is converted into a salt with a nitroalkane show performance equivalent to solvent-borne primers (86). The salt acts as an emulsifier and after application the nitroalkane evaporates, freeing the amine to react with the epoxy resin.

The U.S. Air Force has sponsored a major research program to develop chromate free corrosion resistant treatments for aluminum. One example of such work is the so-called sol–gel coatings. For example, aluminum is treated with a combination of tetraethyl orthosilicate and 3-aminopropyltriethoxysilane. Presumably the tetraethylorthosilicate forms Al–O–Si bonds at the surface and the aminosilane reacts with other OH groups from the silicate to provide amino groups substitution. The amine groups can react with the epoxy resins in the primer to provide adhesion between the primer and the treated metal surface. Reference (87) is a review of work on sol–gel treatments.

Another type of organically modified silicates prepared by hydrolysis of tetramethoxysilane and 3-glycidyloxypropyltrimethoxysilane using diamines such as ethylene diamine as a cross-linker has been studied as corrosion resistant coatings for aluminum (88). In another study, the effect of the ratio of water to tetramethylsilane and 3-glycidyloxypropyltrimethoxysilane in preparing a organically modified silicate was studied; it was found that relatively low ratios of water gave superior corrosion protection to aluminum (89).

Another approach has been the use of electrically conductive polymer coatings on aluminum. Aluminum coated with poly(3-octyl)pyrrole and topcoated with a urethane topcoat has shown promising results in preliminary evaluations (90). Hybrid organic/inorganic corrosion inhibiting pigments, such as $Zn(NCN)_2$/$Zn(2\text{-mercaptobenzothiazole})_2$ have been reported to give equal performance to strontium chromate (48,49).

5. Evaluation and Testing

There is no laboratory test available that can be used to predict corrosion protection performance of a new coating system. This unfortunate situation is an enormous obstacle to research and development of new coatings, but it must be recognized and accommodated.

Use testing is the only reliable test of a coating system—ie, to apply it and then observe its condition over years of actual use. The major suppliers and end users of coatings for such applications as bridges, ships, chemical plants, and automobiles have collected data correlating performance of different systems over many years. These data provide a basis for selection of current coatings systems for particular applications. They also provide insight into how new coatings could be formulated to improve chances of success.

Simulated tests are the next most reliable for predicting performance. One common approach is to expose laboratory prepared panels on test fences in inland south Florida or on beaches in south Florida or North Carolina. The difficulties in developing tests to simulate corrosion in marine environments are discussed in (91). Test conditions must simulate actual use conditions as closely as possible. For example, exposure at higher temperatures may accelerate corrosion reactions; however, oxygen and water permeability can be affected by $(T-T_g)$. If actual use will be at temperatures below T_g, but the tests are run above T_g, no correlation should be expected.

Variables in preparation of test panels are frequently underestimated. The steel used is a critical variable (92). Also significant are how the steel is prepared for coating and how the coating is applied. Film thickness, evenness of application, flash off time, baking time and temperature, and many other variables affect performance. Results obtained with carefully prepared and standardized laboratory panels can be quite different than results with actual production products. In view of these problems, it is desirable, when possible, to paint test sections on ships, bridges, chemical storage tanks, etc, and to observe their condition over the years. The long times required for evaluation are undesirable, but the results can be expected to correlate reasonably with actual use.

Since wet adhesion is so critical to corrosion protection, techniques for studying wet adhesion can be very useful. *Electrochemical impedance spectroscopy* (EIS) is widely used to study coatings on steel. Many papers are available covering various applications of EIS; (93) and (94) are reviews that provide extensive discussion of the theory and interpretation of data. Impedance is the apparent opposition to flow of an alternating electrical current and is the inverse of apparent capacitance. When a coating film begins to delaminate, there is an increase in apparent capacitance. The rate of increase of capacitance is proportional to the amount of area delaminated by wet adhesion loss. High performance systems show slow rates of increase of capacitance, so tests must be continued for long time periods. Onset of delamination can be determined by EIS studies (95). As with many tests of coatings, results of EIS tests are subject to considerable variation; it has been recommended that a minimum of five replicate tests should be run (96). The method is very sensitive for detecting defects, but no information is obtained as to whether the defect is characteristic of the coating system or a consequence of poor application. A series of other problems involved in EIS are discussed in (97). The use of EIS, scanning acoustic microscopy (SAM), scanning vibrating electrode technique (SVET), and energy dispersive X-ray spectroscopy in studying blister formation of coatings on steel has been reported (98).

There have been many attempts to develop laboratory tests to predict corrosion protection by coatings, and these efforts continue. However, available tests have limited reliability in predicting performance; nonetheless, they are widely used. The most widely used test method for corrosion resistance is the salt spray (fog) test (ASTM Method B-117-95). Coated steel panels are scribed (cut) through the coating in a standardized fashion exposing bare steel and hung in a chamber where they are exposed to a mist of 5% salt solution at 100% relative humidity at 35°C. Periodically, the nonscribed areas are examined for blistering, and the scribe is examined to see how far from the scribe mark the coating has been undercut or has lost adhesion. It has been repeatedly shown that there is little, if any, correlation between results from salt spray tests and actual performance of coatings in use (99–103).

Many factors are probably involved in the unreliability of the salt spray test. Outdoor exposure can have a significant effect on film properties, and environmental factors such as acid rain vary substantially from location to location. The application of the scribe mark can be an important variable; narrow cuts generally affect corrosion less than broader ones. Also, if the scribe mark is cut rapidly, there may be chattering of cracks out from the main cut, whereas slow cutting may lead to a smooth cut. A passivating pigment with high solubility might be very effective in a laboratory test, but may provide protection for only a limited time under field conditions, owing to loss of passivating pigment by leaching.

Since with intact films, it is common for the first failure to be blister formation, humidity resistance tests are also widely used (ASTM Method D-2247-94). The face of a panel is exposed to 100% relative humidity at 38°C, while the back of the panel is exposed to room temperature. Thus, water continuously condenses on the coating surface. This humidity test is a more severe test for blistering than the salt fog test because pure water on the film generates higher osmotic pressures with osmotic cells under the film than the salt solution used in the salt fog test. It is common to run the test at 60°C "because it is a more severe test". The pitfalls of this approach are obvious in view of the previous discussion of the importance of ($T - T_g$). Humidity tests do not predict the life of corrosion protection, but may provide useful comparisons of wet adhesion. Wet adhesion can be tested by scribing panels after various exposure times in a humidity chamber, immediately followed by applying pressure sensitive tape across the scribe mark, and then pulling the tape off the panel. A peel adhesion test for wet adhesion has been described (104). Wet adhesion can also be checked after storing panels in water (105).

It is often observed that alternating high and low humidity causes faster blistering than continuous exposure to high humidity. A possible explanation of this is that intermediate corrosion products form colloidal membranes, causing polarization and temporary inhibition of corrosion. The membranes are not stable enough to survive drying out and aging. Another factor may be the increase in internal stress that has been reported by cycling through wet and dry periods (34). A large number of humidity cycling tests has been described, commonly involving repeated immersion in warm water and removal for several hours. In some industries, such tests have become accepted methods of screening coatings, although their predictive value is questionable. Simply correlating them with salt fog tests proves little.

A testing regimen called *Prohesion* has been reported to correlate better with actual performance than the standard salt spray test (106). The procedure combines care in selection of substrates that will reflect real products, use of thin films, emphasis on adhesion checks, and a modified salt mist exposure procedure. Instead of 5% NaCl solution, a solution of 0.4% ammonium sulfate and 0.05% NaCl is used. Scribed panels are sprayed with the mixed-salt solution cycling over 24 h, six 3-h periods alternating with six 1-h drying periods using ambient air. During these cycles, water can penetrate through the film to a greater extent than in salt fog chamber testing in which the humidity is always at 100% and the 5% salt solution minimizes water penetration because of reverse osmotic pressure. The importance of the effect of weathering on corrosion protection has been emphasized. Including a QUV exposure cycle in the cycling regime is said to improve the reliability of accelerated testing (107). Another cycling test in which the automotive industry is gaining confidence is the Society of Automotive Engineers test SAE J-2334.

Neither salt fog nor humidity tests have good reproducibility. It is common for differences between duplicate panels to be larger than differences between panels with different coatings. Precision can be improved by testing several replicate panels of each system. (Commonly, decisions are based on the results from testing two or three panels.) The problem is further complicated by the difficulty of rating the degree of severity of failure. A rating system and an approach to statistical analysis of data have been published (108). The study was based on panels with an acrylic clear coating and a pigmented alkyd coating (neither coating would be expected to have good corrosion protection properties) exposed to 95% relative humidity at 60, 70, and 80°C. The times to failure were extrapolated down to ambient temperatures. In light of the effect of T_g on permeability, the validity of such extrapolations is doubtful.

A further problem of evaluating panels for corrosion protection is the difficulty of detecting small blisters and rust areas underneath a pigmented coating film without removing the film. Infrared thermography has been recommended as a nondestructive testing procedure (39).

A great deal of effort has been expended on electrical conductivity tests of paint films and electrochemical tests of coated panels. [See (109) for an extensive review.]

A variety of cathodic disbonding tests specifically for testing of pipeline coatings has been established by ASTM: G-8-96, G-42-96, and G-80-88 (reapproved 1992). In these tests, a hole is made through the coating and the pipe is made the cathode of a cell in water with dissolved salts at a basic pH. Disbonding (loss of adhesion) as a function of time is followed. While there is considerable variability inherent in such tests and their utility for predicting field performance is doubtful, useful guidance in following progress in modifying wet adhesion may be obtained. Such tests may be used more broadly than just for pipeline coatings. For a discussion of research on cathodic delamination, including investigation of the migration of cations through or under coating films, see (110).

The lack of laboratory test methods that reliably predict performance puts a premium on collection of databases permitting analysis of interactions between actual performance and application and formulation variables. It is especially critical to incorporate data on premature failures in the database. Availability of such a database can be a powerful tool for a formulator and may be especially useful in testing the validity of theories about factors controlling corrosion. In time, it may be possible to predict performance better from a knowledge of the underlying theories than from laboratory tests. Many workers feel this is already true in comparison with salt fog chamber tests.

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