Barrier Coatings

by Clive H. Hare, *Coatings System Design Inc.*

The next several columns will use previously reviewed fundamentals of corrosion control, including corrosion science, permeability, and blistering of coating films on metal to provide an understanding of coating design precepts for corrosion control. Simultaneously, the discussion will address the difficulties that are specifically related to the practical formulation, use, and service of these coatings.

Of the various ways in which the corrosion process might theoretically be manipulated (or thwarted) by the use of coatings, only 3 techniques have led to practical solutions (Table 1): barrier coatings, inhibitive pigments, and cathodic protection. Barrier techniques include the deprivation of fuel for the cathode reaction and/or the maximization of electrolytic resistance at the interface.

The inhibitive process entails modifying the underfilm environment to chemically inhibit the susceptibility of the metal to corrode. In cathodic protection, coatings are used as electrically contiguous anodes, which override local cell action on the steel substrate and prevent all current discharge from the metal.

This article will discuss the function of barrier coatings and the design of barrier primers and finishes.

Table 1
Practical Strategies for Corrosion Control by Coatings

Oxygen Deprivation	Barrier Coatings	Cathodic reaction is controlled by coating preventing access of oxygen to the metal.
Resistance Inhibition	Barrier Coatings	Rate of corrosion is minimized by ensuring interface between coating and steel maintains very high electrical resistance. Coating prevents access of soluble ions to metal.
Environmental Modification at Interface	Inhibitive Primers	Passivation of metal is induced by introducing oxidizing or non-oxidizing passivating ions into interfacial electrolyte against metal. Modification of pH may be employed to decrease level of oxygen and/or inhibitive ion necessary to acquire passivity.
Cathodic Protection	Zinc-Rich Primers	Prevention of current discharge from steel to electrolyte by electrical attachment of less passive anode (zinc metal) which in presence of continuous electrolyte renders steel entirely cathodic and overrides all local cell action on steel surface. Active metal (zinc) corrodes, and sacrificially protects steel.

Mechanisms for Corrosion Protection by Barrier Coatings

Barrier coatings are the most straightforward of the 3 basic types of coatings for corrosion protection. They use none of the exacting pigmentary devices of inhibitive primers and zinc-rich films, and pigment volume concentration/critical pigment volume concentration (PVC/CPVC) ranges are less critical. While suitable pigmentation enhances barrier protection, barrier coatings derive their value primarily from the impermeability of the organic binder. The major requirements are to minimize the access to the metal of fuel for the cathodic reaction and to maximize the electrical resistance of the external phase of any likely corrosion cell.

Resistance Inhibition

For many years, it was believed that barrier coatings might function by excluding water and oxygen from the metal. This belief was soundly disputed when, in the early 1950s, J.E.O. Mayne[1] measured the amount of water and oxygen passing through "normal" 4-mil (100-micrometer) paint films. He found water and oxygen levels to be much higher than the levels needed to initiate and sustain the average rate of corrosion on unprotected steel. On coated steel, he found levels of 200-

continued

Copyright ©1998, Technology Publishing Company

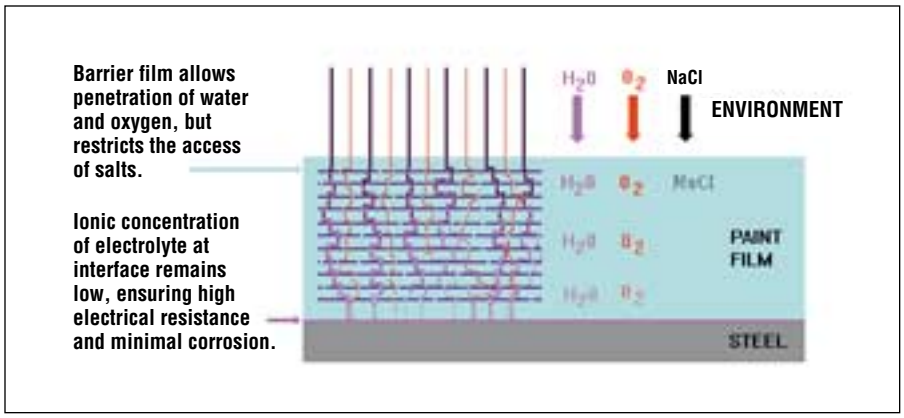


Fig. 1 - Corrosion control by barrier coatings (resistance inhibition)

1,100 mg/cm^2/year (0.045-0.25 oz/in.^{2}/year) of water and 4-53 mg/cm^2/year (0.0009-0.012 oz/in.^{2}/year) of oxygen. The 70 mg/cm^2/year (0.016 oz/in.^{2}/year) rate of corrosion typical of bare steel required only 11 mg/cm^2/year (0.002 oz/in.^{2}/year) of water and 30 mg/cm^2/year (0.007 oz/in.^{2}/year) of oxygen—appreciably less than levels passing through the films. The latter figures are in reasonably good agreement with those of Baumann, quoted by Haagen and Funke[2], i.e., 0.003-0.06 mg H_2O/cm^2/day (1.1-1.2 mg/cm^2/year) and 0.008-0.15 mg O_2/cm^2/day (2.9-54.7 mg/cm^2/year) required to sustain a daily rate of corrosion of 0.02-0.25 mg Fe/cm^2 (7.3-91.2 mg/cm^2/year).

Despite these discouraging data, it was indisputable that paint films that did not have inhibitors or sacrificial pigments provided adequate corrosion protection to steel for years. Mayne[1] proposed that these films could control corrosion by maintaining a high electrical resistance at and above the interface, thereby preventing external current flow between anodic and cathodic areas on the underfilm metal. Mayne[1] cited the high ionic impermeability of well-prepared coating films.

This would ensure that water in the film that could access the interface would not be conductive enough to carry appreciable corrosion current (Fig. 1). The film had to be continuous, have high electrical resistance, and be free of any ionogenic material that might short-circuit the resistance. (The DC resistance of typical protective coatings is about 10^{10}ohms•cm^2, although it will drop to about 10^8ohms•cm^2 where continuous aqueous pathways through the films exist.) It was also critical that the interface be free of soluble ionic contamination.

Described in the *JPCL's* November 1997 Trouble with Paint (p. 80), the work of Mayne and his co-workers on the behavior of paint films with regard to the take-up of ionic material and film conductivity has direct bearing on the design of barrier systems. Minimizing film areas with D-type conductivity becomes critical to good barrier performance, which relies on resistance inhibition. Therefore, eliminating areas of low cross-link density in thermosetting systems would appear to be an important formulating goal. Similarly, in thermoplastics, highly amorphous areas are probably less effective in preventing corrosion current than are more crystalline areas.

Both formulating requirements have disadvantages. Highly cross-linked films incur higher internal stress values and diminished mechanical properties. High crystallinity in thermoplastics leads to reduced solubility, higher volatile organic compound (VOC) content, and reduced mechanical properties. How-

Copyright ©1998, Technology Publishing Company

ever, the reduction of free volume; T_g elevation; and the elimination of monofunctional and non-functional diluents, monomers, and plasticizers are productive formulation design stratagems. Even monofunctional diluents may not react entirely into the polymeric matrix, and their volatilization from films in high temperature service is likely. Cross-link density and ultimate tensile strength can be maximized by avoiding leachables and hydrophilic pigmentations, improving solvent release, and incorporating long periods of drier inductions before application of oxidizing films. These techniques also minimize water uptake and the amount of D-type conductivity. Eliminating water- and ion-attracting groups on the polymer, such as hydroxyls and carboxylic acid groups, also helps minimize D-type conductivity. However, valuable benefits can be derived from these same groups, at least in barrier primers (see below).

Oxygen Deprivation

As a mechanism for barrier protection, resistance inhibition is not without its detractors. As Wicks[3] has pointed out, while high resistance films are certainly much more protective than films of low resistance, there is less correlation of resistance and protection in quantitative comparisons of performance in films having different levels of high resistance. Moreover, in recent years, economics and the press of environmental controls have forced changes in the practice of only applying barrier films to clean, well-blasted surfaces. We now have to apply barrier coatings (e.g., aluminized epoxy mastics and moisture-curing urethanes) directly over highly questionable surfaces known to bear soluble salt, especially chlorides and sulfates, which produce conductive and highly corrosive electrolytes. Surprisingly, when applied at sufficient film thickness, these barrier systems have worked well in some instances. Resistance inhibition cannot in this case be the underlying mechanism of protection. The film excludes ionic material from the environment external to the coating system. But deionized water accessing the substrate through the paint film finds enough salts at the substrate to produce a low resistance and presumably aggressive corrosive environment (Fig. 2). Thus, other factors must be involved.

In 1970, Guruviah[4] studied the rates of water and oxygen permeability through several iron oxide-pigmented films and related these to the performance of the same system

continued

Copyright ©1998, Technology Publishing Company

in salt spray and humidity. Guruviah found some limited correlation between weight loss values observed on the exposed panels and values calculated on the assumption that oxygen permeability was the rate-determining step. Guruviah concluded that corrosion rates could be interpreted by the oxygen permeability data (Fig. 3). Baumann[5], Haagan and Funke[2], and later Thomas[6] have all found that many paint films have oxygen permeability rates below or close to the rates required to sustain corrosion resistance.

Of even more relevance to the question of whether the mechanism is resistance inhibition or oxygen deprivation may be the 1990 study of Morcillo et al.[7] They investigated the effects of increased loadings of NaCl and $FeSO_4$ (as well as mixtures of the 2 salts) on lightly adherent, thin-film, varnish-coated steel. Morcillo found that corrosion, which did not occur on non-contaminated steel, increased as interfacial contamination increased. This suggests that resistance inhibition was the controlling factor on clean steel at low salt concentration levels. As levels of contamination increased, however, the estimated consumption of oxygen required for a quantified degree of underfilm corrosion equated more closely with the oxygen permeability data. Morcillo concluded that under these circumstances (i.e., high salt levels at the interface and a water-permeable film), oxygen permeability was the controlling factor.

Unfortunately, at this time, the amount of available oxygen permeability data correlatable to known quantitatively measured coating performance is sparse. In addition, results are complicated by other effects. Changes in oxygen transmission that occur with the simultaneous absorption of water and the effects of temperature may have a considerable effect. The issue, therefore, remains to be decided. Both mechanisms may be involved, especially in high builds of modern barrier systems (e.g., aluminized epoxies, coal tar epoxies, epoxy phenolics, vinyl esters, and unsaturated polyesters).

Wet Adhesion

Funke[8] argues that although water permeability may not be the rate-determining step in corrosion, an electrical corrosion cell beneath a dense barrier film cannot become established until there is a continuous aqueous phase across the metal surface. Funke cites de-adhesion under water-wet conditions as the primary factor in the onset of corrosion; wet adhesion, therefore, is the paramount design criterion in the formulation of barrier coatings. While it is

continued

Copyright ©1998, Technology Publishing Company

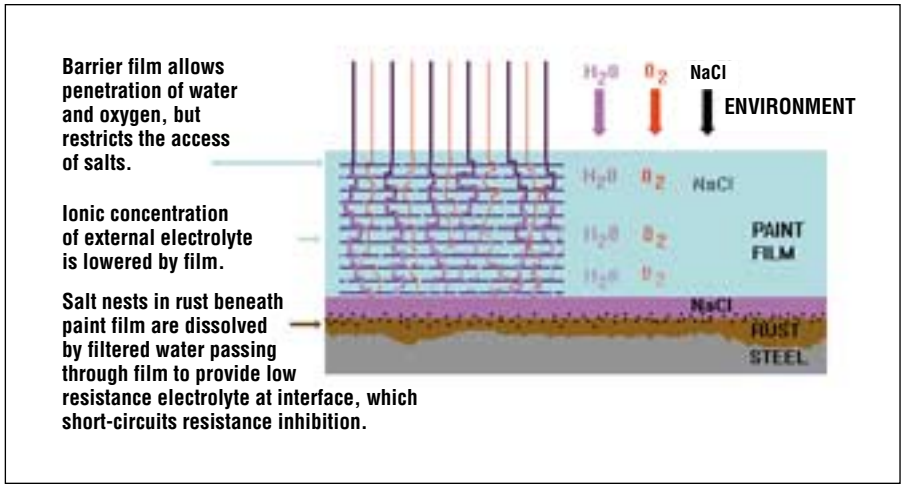


Fig. 2 - Effect of interfacial salt deposits on resistance inhibition by barrier films

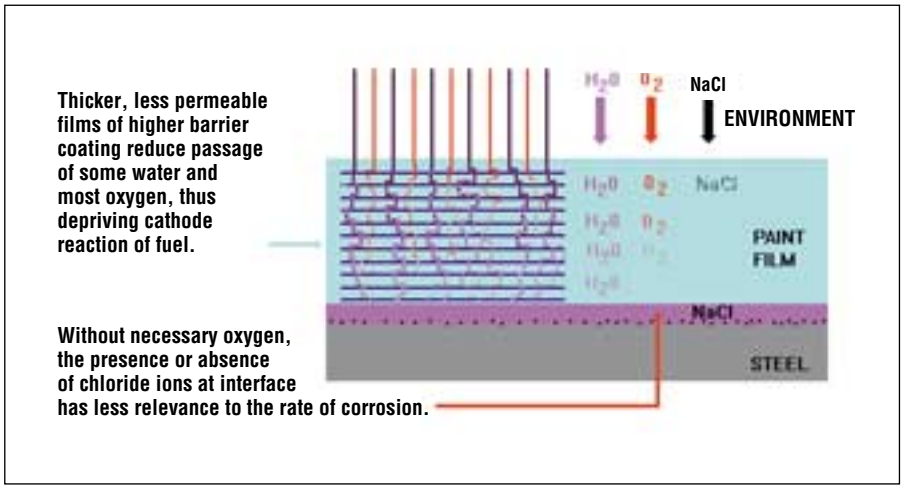


Fig. 3 - Corrosion control by barrier coatings (oxygen deprivation)

theoretically possible that a highly porous film may become so waterlogged that a continuous electrolytic path may exist within a still adherent coating, such films are altogether inappropriate as barrier systems.

Wet adhesion may have little relationship to dry adhesion. Indeed, the site and type of parting may be quite different. Wet adhesion loss is usually 100 percent adhesive. Delamination of the dry film on steel is as often cohesive, occurring in a weak boundary layer within the coating film next to the interface.[9]

Barrier Primer Design

Binders

Uncompromising adhesion under wet service conditions is the primary formulating goal for the barrier primer, more so in fact than absolute impermeability. Sound, uncontaminated surfaces with maximized surface area through chemical or physical scarification are necessary for good adhesion. But adhesion also depends on the physiochemical properties of the binder and good wetting properties. In addition, adhesion depends on the interfacial alignment of polar groups on the coating binder (hydroxyls and carboxylic acid groups) with polar and hydrophilic oxides and hydroxides on the metal surface. Thus, maximized adhesion of the barrier primer depends on increased polar groups on the binder. To displace air from all facets of a steel surface, the wet primer must be low

continued

Copyright ©1998, Technology Publishing Company

enough in surface tension and viscosity. On blast-cleaned surfaces, displacing air may be difficult, for the coating must access the pits and crevices of the blast pattern. Failure to properly wet the steel reduces the adhesion of the cured film, and leaves non-bonded sites beneath the film available for the subsequent accumulation of water in service.

Unfortunately, the polar groups (which facilitate wetting) are precisely the same groups that attract water into the film, displacing the barrier from the substrate. In addition, polar groups may actually reduce oxygen impermeability, which is more productively controlled than water impermeability.

For de-adhesion to occur, the water must displace multiple interfacial polar linkages simultaneously. This action becomes difficult if the polar groups are well aligned on a stiff, immobile polymer chain and the film temperature is below the T_g.[10] If, however, the binder is made up of very flexible chains with relatively poor alignment after film formation and the film is above its T_g, then interfacial bonds between polymer and surface will be continuously formed and broken. Here, water molecules may more readily associate with polar groups and progressively deprive the film of its necessary bonding potential. Molecular motion inevitably increases with temperature, especially above the T_g. For this reason, maximizing the T_g is important in binder selection. At a minimum, T_g must be above the service temperature. In a series of experiments with the Navy's epoxy polyamide barrier coating, MIL-P-24441, blister resistance could not be achieved in a 190 F (88 C) immersion test. When a cycloaliphatic amine curing agent of relatively higher T_g was substituted for the polyamide originally used, blistering resistance was extended from an original six-day exposure to greater than 10 months, the point at which the test was discontinued.[11]

While the polarity of the binder in a barrier coating is, in part, a positive attribute, other factors have adverse effects on performance. Other hydrophilic formulation constituents will inevitably associate with water, increasing the water absorptivity of the film and introducing the danger of osmotic blistering in fresh water after recoating. If water can hydrolyze the binder (especially in the presence of cathodic alkalis), the polymeric binder will be broken up or even dissolved. Reaction products of the hydrolysis of esters are alcohols and acids, and these will pull more water into the film. All of these things produce catastrophic film breakdown and complete collapse

continued

Copyright ©1998, Technology Publishing Company

of barrier properties and adhesion. Blistering will be both osmotic and cathodic. Ester groups are particularly vulnerable because of their sensitivity to alkaline-induced hydrolysis. They are not generally desirable in barrier coatings. As alkali is generated by the cathode reaction, the binder becomes vulnerable to this type of attack, leading to delamination of the film from cathodic sites and saponification and increased water sensitivity in the polymer. Fortunately, not all ester linkages suffer from the same degree of susceptibility to alkali attack. While the fatty acid triglycerides in oil paints are extremely sensitive, ester linkages in many polyester resins are unusually resistant. Other groups, including amides, ureas, and urethanes, may also show diminished resistance to cathodic alkali.

Solvents

Solvents, pigments, surfactants, and minor ingredients, as well as high boiling solvents, should also be selected with thought to their effect on barrier properties. Water-miscible alcohols, glycol ethers, and esters (especially those with high boiling properties) should not be used as solvents. If entrapped within the film, these materials can cause severe blistering in immersion service and may leach into and contaminate the contents of vessels when used as container coatings or linings for food and water storage. Under conditions of extreme high or low pH, certain solvents such as esters will hydrolyze to the acid. Ester solvents, for example, should not be used with the amine or amide curing agents of epoxy coatings. Eliminating esters from the formulation would also minimize post-curing hydrolysis of retained solvent residues.

Small, compact, planar, and short-chained solvents are released from the film faster than the bulky,

continued

Copyright ©1998, Technology Publishing Company

branched, or non-planar molecules during the final diffusion stages of solvent release. These solvents should be used wherever possible. Furthermore, the release of polar solvents from the film will be more substantially retarded in highly humid environments than non-polar solvents. Solvent selection largely depends on binder selection. It may not be entirely possible to avoid the use of all such materials without preventing resin precipitation. Wherever possible, however, the polar carriers should be the low boilers (e.g., methyl ethyl ketone), and the tail solvents should be efficient non-polar materials (high flash naptha) or polar solvents with minimal water miscibility (methyl amyl ketone instead of propylene glycol monomethyl ether acetate, for example).

Pigments

Lamellar pigments are a valuable device to reduce permeability in all coatings. Discussed in more detail under Design of Barrier Finishes, they also may be effectively used in barrier primers. Environmentally reactive pigments (calcium carbonate, iron blue, and the chromates) as well as highly soluble inhibitive pigments should not be used in barrier systems, although careful use of very low solubility modified phosphates may be successful. Flat, platy pigments may also be valuable in mitigating the negative effects of internal and external stress accretion. Given enough stress, the films will delaminate.

Effect of Mobility and Film Thickness

Although molecular immobility after cure is critical to maintaining the wet adhesion of the dried film, a high degree of molecular mobility in the wet film is equally critical to the initial establishment of adhesion. High mobility during the wet stage (i.e., before drying or at least curing) is critical for the film to properly access and wet all facets of the metal surface and displace atmospheric moisture. Conversion from the mobile state to the rigid film should also involve minimal levels of stress accretion, allowing maximum stress relaxation. Two disadvantages of rapid conversion from the wet to fully cured stage are increased internal stress and reduced adhesion. In some cases, rapid conversions cause spontaneous delamination of highly cross-linked systems. The slow conversion rates of oil paints and a consequent, almost complete, dissipation of stress contribute to the excellent initial adhesion of these systems. However, oil paints represent the extreme example. The same slow progress of cure in oil paints from the wet film to the immobile state is too long to optimize impermeability in practical barrier systems.

Minimizing film thickness with low-solids, high-wetting primers is also a viable technique in curbing stress accretion during conversion, although here a high surface profile and the drainage of the coatings from the peaks to the valleys are clearly counterproductive. In pretreatment coats, such as the wash primer, low film thickness plays some part in increased adhesion.

Increasing film thickness is, however, a primary tool for creating a viable barrier system. In heavy-duty coating systems, there is some film thickness threshold (commonly 16-20 mils [400-500 micrometers]) above which a disproportionate increase in corrosion resistance is realized.[3] Once system adhesion has been established through optimal primer design, subsequent coats may be applied at higher film thickness. The transmission of water vapor or oxygen through all films decreases as film thicknesses in-

continued

Copyright ©1998, Technology Publishing Company

crease, as long as the film is uniformly cured. Blistering is decreased as film thickness increases.[12] Multiple coats are crucial, in spite of the cost disadvantages of this approach and the theoretically increased possibility of problems at newly created interfaces between coats. Too many coating failures result from holidays, pinholes, and insufficient film thickness over high points in the steel surface. Paint jobs improve as the statistical probability of holidays in any coat is countered by the application of 2 coats; and 3 coats are better than 2.

Pinholes and holidays may be particularly bad on once-corroded steel, where even after abrasive blasting, the surface may be very irregular and deeply pitted. Single- or even double-coat applications on these surfaces are often doomed because of the difficulties in ensuring coverage of all profile peaks (Fig. 4) and the high number of pinholes generated by incomplete wetting of the pits and porosities. Unless the coating is slow-drying and very low in viscosity, it will have difficulty displacing air from the pit cavities and retaining sufficient flow to prevent bubbles, pinholes, and craters from forming in the drying film. The phenomenon is similar to that found when recoating inorganic zinc films with fast-drying high viscosity coatings. (Air that is displaced from the pits by the finish may not be able to be entirely released through the fast-drying finish. This results in bubbles and pinholes in the finish.) Low viscosity does not equate well with high solids in modern coating materials, nor with the requirement for high film thickness. The saturation of a surface with a high-wetting sealer, followed by 1 or 2 (or preferably more) coats of a higher build intermediate and finish coating, will better address the problem.

Internal stress buildup is also minimized in systems built up of 2 or 3

Copyright ©1998, Technology Publishing Company



Fig. 4 - Poor coverage of profile peaks in both a zinc-rich primer and a polyurethane finish resulting in premature areas of patchy zinc and ferric corrosion.

coats, rather than a single coat applied at the same film thickness. Intensified internal stress effects from film formation of high-build thermosets are the biggest disadvantages in the design of high-build barrier systems. Excessive film thickness in solvent-borne systems is often tempered by an awareness of the danger of plasticization, increased transmission properties, blistering, and, in closed spaces, the buildup of vapors long after application. The introduction of 100 percent solids systems such as epoxies, vinyl esters, and saturated polyesters has removed these concerns, encouraging the application of higher film thicknesses in a single coat. Some 100 percent solids systems (namely acrylics, vinyl esters, and unsaturated polyesters) exhibit very high shrinkage on polymerization, maximizing internal stress. In epoxies and especially in polyurethanes, stress buildup either is lower or is dissipated more readily.

Even under controlled conditions, multi-coat applications of thinner films of solvent-borne barrier coatings give lower oxygen permeability coefficients than do thicker film single-coat applications on the same substrate.[2] This property is again thought to be related to the effects of solvent entrapment.

Design of Barrier Finishes

Binder

The design of barrier binders for intermediate and finish coats is different from the design of the primer polymer. Adhesion between organic systems in all films above the primer or pretreatment is easier to achieve than adhesion between the organic primer and the steel. In barrier finishes and intermediate coats, therefore, adhesion becomes secondary to maximizing impermeability.

Polymers for barrier intermediate and finish coats with carbon-carbon, carbon-nitrogen, and carbon-ether linkages are, therefore, preferred to those systems based on polymers with many hydroxyl and carboxylic acid groups. In non-exposed finishes and mid-coats, aromatic groups are included in these preferred moieties. Highly uniform cross-link density in thermosets and ordered, well-aligned chains in thermoplastics are desirable. The chlorinated thermoplastics (vinyls and chlorinated rubbers) make excellent barrier systems because of the high degree of secondary valency attractions throughout the polymer matrix.

T_g is critical in barrier primers and finish coats alike, for water absorption and, in consequence, oxygen absorption increase significantly as the ambient temperature (T) becomes greater than T_g.

Pigmentation

Ideally, pigment selection will augment the choice of binder and lead to enhanced performance under severely corrosive conditions. It may also play a large part in system fail-

continued

Copyright ©1998, Technology Publishing Company

ure. Suitable pigments are flat, platy materials, such as aluminum and stainless steel metallic flake. Micaceous iron oxide and glass flake are also used. Graphite, which has been used in barrier systems, is described by Svoboda and Mleziva[13] as stimulating corrosion. Extender systems of similar platy geometry will control gloss and PVC/CPVC ratios where necessary. These systems include mica, talc, and chlorite. Mica is highly absorbent and will rapidly lower CPVC levels. It may also easily flocculate the pigment system; therefore, levels should be controlled judiciously. PVC/CPVC should not affect permeability significantly as long as it does not get too high. Generally, it should be kept below 0.5-0.6.

Platy pigments require extra care with film thickness because solvent entrapment effects may be magnified. This is especially true with leafing aluminum pigments, which are designed to accumulate predominantly at the upper surface of the film parallel to the substrate, further enhancing barrier properties. Low surface energy of leafing aluminum pigments is ensured by the surface treatment of the pigments with stearic acid. In suitable high-leafing (higher energy) binder systems, these pigments may actually leaf out of the film, so that a loose aluminum layer is present on top of the film. Thus, this pigment should be used only in the finish coat to avoid intercoat adhesion problems. It may even be necessary to remove loose material from the surface in maintenance repainting. However, chalking residues from the degradation of the binder are minimized when leafing aluminum pigments are used.

In many high-performance systems, viscosities are high, and too many components deleaf aluminum, thereby eliminating the leafing tendency. Often, non-leafing aluminum pigments are used in these systems. While also orienting parallel to the substrate, these pigments are more homogeneously distributed throughout the film depths and cause no recoating difficulties.

Entrapped solvent (especially hydrophilic solvent) within the film can lead to osmotic blistering. In moisture-curing urethanes, metallic pigments (particularly the leafing aluminums) can cause increased gas (CO_2) bubble entrapment in the film. This entrapment not only reduces the permeability of the film but also endangers its aesthetics.

Silane surface-treated grades of wollastonite are effective in barrier systems (because of some degree of increased bonding between pigment and binder). Similar treatments on

continued

Copyright ©1998, Technology Publishing Company

other pigments may further improve performance of barrier coatings.

Loadings of metallics are best controlled to something near 15 PVC. Care is necessary when using metallic pigments with electrical potentials less active than steel (e.g., stainless steel flake and nickel flake) to maintain pigmentation levels well below the point at which the film becomes conductive. In this way, we may eliminate the possibility of pitting in the steel substrate at pinholes or holidays because of unfavorable cathode-anode ratios.

Intercoat Adhesion

Thermosetting coatings usually have a finite recoat window for applying final or intermediate coats to the previous layer. This window is related to the proclivity of the curing primer (or intermediate) to be softened or partially dissolved by the subsequent coat, an effect which enhances adhesion. This recoat window in thermosets such as epoxies diminishes as primer cure advances and most usually as temperature increases. In thermoplastics, the recoat window is virtually infinite. This characteristic is of singular value in repair and renovation of old systems.

However, intercoat adhesion can plague barrier systems based on thermosetting systems such as polyurethanes and epoxies (especially coal tar epoxies and amine-cured systems). While these problems may often be traced to poor application practices or even to formulating practices, intercoat adhesion problems may be simply related to the nature and gloss of the film. After curing, films of higher crosslink density develop surfaces that are hard and often glossy. These surfaces are extremely difficult to recoat without subsequent adhesion problems. Certain polymers form unexpectedly inhospitable films that are difficult to recoat. Oil-modified urethane films, for example, may be impossible to recoat successfully without sanding after a 24-hour intercoat interval.

Certain flow control and anti-cratering agents such as those based on dimethyl silicone fluids may also cause adhesion problems when used in primers and intermediate coats. Polyalkylene oxide modified silicones having improved compatibility with the binder have less negative effect on intercoat adhesion.

The recoat windows of many systems are short, especially under high temperature conditions. These intercoat adhesion problems, normally demanding some mechanical scarification between coats, may become more important as existing (and

Copyright ©1998, Technology Publishing Company

now commonly used) polyurethane and epoxy maintenance systems need repainting. Where solvent resistance properties are not essential, it may be possible to deliberately modify base coats with thermoplastic modifiers that can be softened or even partially dissolved in the solvents of the recoat. In this way, gloss-on-gloss applications without mechanical or chemical scarification may be made and continued in maintenance practices without adhesion failure. The device is not terribly different from that used to achieve adhesion to certain oleofinic plastics. It has, for example, been used extensively in marine applications. Atherton[14] reports that this type of system has given good service for 15 years or more. The author has used low molecular weight vinyl resins in epoxy coatings to upgrade intercoat adhesion.

Intercoat adhesion in thermosets may be improved by selecting primers and intermediates or intermediates and finish coats so that primary bonds may be formed between reactive groups in one coat and complementary groups in another coat. Slight excess in the amine functional groups of an epoxy primer may be used to react with isocyanate groups in a finish coat, thereby increasing the chemical bonding across the interface. In some cases, intercoat adhesion has been improved by deliberately offsetting stoichiometries in interfacing coats.

In some primer coats, added "tooth" has been built in by including relatively coarse extenders (e.g., diatomaceous silica). Such extenders provide rougher films and give improved anchorage of subsequently applied intermediate and finish coats. While the technique has been used in inhibitive epoxy metal primers on bridges in Texas, the use of such coarse aggregates (especially diatomaceous silica) is not optimally suited to barrier systems. The technique must be used very carefully, or it will affect permeability.

Holidays and Bare Spots

Without either passivating or sacrificial pigments, barrier films offer no protection to steel at bare areas. The coatings are normally dense, abrasion-resistant, and not easy to damage. Film disruptions do occur, however, and the universal possibilities of pinholes and holidays are hardly avoidable. In high-build applications of low permeability coatings where such sites are small, corrosion and blistering do not proceed aggressively. However, in film sections thin enough to allow the transmission of oxygen, cathodic blistering adjacent to defective (anode) sites can occur

continued

Copyright ©1998, Technology Publishing Company

when films have insufficient hydrolytic resistance.

At cut scribes and other sites of significant damage, corrosion cells may be set up between the exposed anodic steel at the damaged area, where corrosion builds up, and at cathodes at the periphery of the damage, where oxygen is available more abundantly through the adjacent paint film.[10,15] At the edge of the defect, the alkaline condition developed by the cathode reaction may loosen the paint adhesion directly. In films of sufficient alkali sensitivity (e.g., films containing ester groups, amides, urethanes), the film against the interface may actually be destroyed by hydrolysis. Phosphate conversion coatings may also be so destroyed.[16] These mechanisms lead to a laterally advancing cathodic front of attack, followed by the anodic rust front as the delaminating film exposes more metal. The phenomenon is known as undercutting. There is evidence from SSPC[17] that undercutting of this type proceeds at linear rates that are dependent upon coating type and the severity of the exposure. The SSPC data[17] also indicate that stress effects may be involved, for undercutting in a three-coat system is found to initiate sooner and advance more rapidly than it does in a corresponding two-coat system.

In the presence of remote but electrically continuous unpainted cathodes, severely unfavorable area ratios (i.e., high cathode arc to anode arcs) can develop in immersion service. These ratios can lead to aggressive pitting. In the presence of cathodic protection in immersion service, cathodic delamination can be a problem around bare spots. Additionally, bare areas will increase the current requirements necessary to maintain an entirely cathodic substrate during cathodic protection, thus increasing protection costs.

It is essential, therefore, to examine these coating systems carefully for discontinuities before job completion. Depending on the film thickness of the coating, either low voltage wet sponge or high voltage (500-200,000 volt) sparking detectors may be used. Areas exhibiting defects must be carefully repaired, and adequate coating thickness must be restored.

Conclusion

Next, we will discuss coatings based on inhibitive metal primers. ❑

References

1. *J.E.O. Mayne, "The Mechanism of Inhibition of the Corrosion of Iron and Steel by Means of Paint,"* Official Digest, *Volume*

Copyright ©1998, Technology Publishing Company

24, Number 127 (1952), 127.
2. *H. Haagen and W. Funke, "Prediction of the Corrosion Protection Properties of Paint Film by Permeability Data,"* JOCCA *(October 1975), 359.*
3. *Z.W. Wicks,* Corrosion Protection by Coatings*, Federation Series on Coatings Technology, Series II (Blue Bell, PA: Federation of Societies for Coatings Technology, 1987).*
4. *S. Guruviah, "The Relationship between the Permeation of Oxygen and Water through Paint Films and Corrosion of Painted Steel,"* JOCCA *(August 1970), 669.*
5. *K. Baumann,* Plaste und Kautschuk *(1972), pp. 455, 694.*
6. *N. Thomas, "Coatings for Rusty Steel: Where Are We Now?"* JOCCA *(March 1991), 83.*
7. *M. Morcillo, L.S. Hernandez, J. Simancas, S.J. Feliu, and S. Gimenez, "Underfilm Corrosion of Steel Induced by Saline Contaminants at the Metal/Paint Interface,"* JOCCA *(January 1990), 24.*
8. *W. Funke, "The Role of Adhesion in Corrosion Protection by Organic Coatings,"* JOCCA *(September 1985), 229.*
9. *See exchange of letters among Peter Walker,* JOCCA *(December 1985), 318; T.R. Bullet,* JOCCA *(February 1986), 44; and Werner Funke,* JOCCA *(March 1986), 78.*
10. *W. Funke, "Towards Environmentally Acceptable Corrosion Protection by Organic Coatings—Problems and Realization,"* Journal of Coatings Technology *(October 1983), 31.*
11. *R.F. Brady and C.H. Hare, "The Development of a High Solids Epoxy Polyurethane Coating Line,"* JPCL *(April 1989), 49.*
12. *C.G. Munger, Corrosion Prevention by Protective Coatings, Chapter 13 (Houston, TX: NACE, 1984), p. 335.*
13. *M. Svoboda and J. Mleziva, "Properties of Coatings Determined by Anticorrosive Pigment,"* Progress in Organic Coatings*, Vol. 12 (1984).*
14. *D. Atherton, "Original and Maintenance Painting Systems for North Sea Oil and Gas Platforms,"* JOCCA *(1979), 351.*
15. *J. Stone, "Paint Adhesion at the Scribed Surface: The PASS Test,"* Journal of Paint Technology*, Vol. 41 (December 1969), 661.*
16. *R.R. Wiggle, A.G. Smith, and J.V. Petrocelli, "Paint Adhesion Failure Mechanism on Steel in Corrosive Environments,"* Journal of Paint Technology*, Vol. 40 (April 1968), 164.*
17. Performance Testing of Marine Coatings*, SSPC 90-02 (Pittsburgh, PA: SSPC, 1990).*

Copyright ©1998, Technology Publishing Company