Blistering of Paint Films on Metal, Part 1: Osmotic Blistering

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This month's column will discuss the practical effects of water absorption into applied coating systems on metal. The article begins a two-unit review of blistering failures and delaminations in terms of the driving forces that produce them. At this stage, our discussion will only address blistering phenomena on metal. While blistering can affect the service of coatings on concrete and other substrates, these will be considered in later segments of this series, when we direct specific attention to the substrates. Blistering or bubbling produced by agents other than water, such as gas- or solvent-induced blistering, will not be considered.

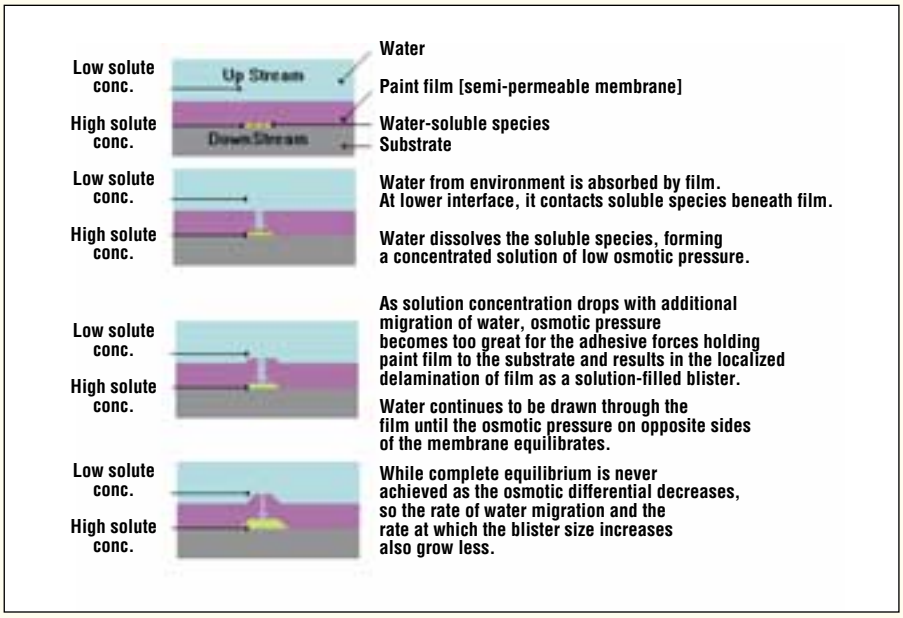


Fig. 2 - Mechanism of osmotic blistering of coating films



Fig. 1 - Osmotic blistering of coating on steel
Figures courtesy of the author

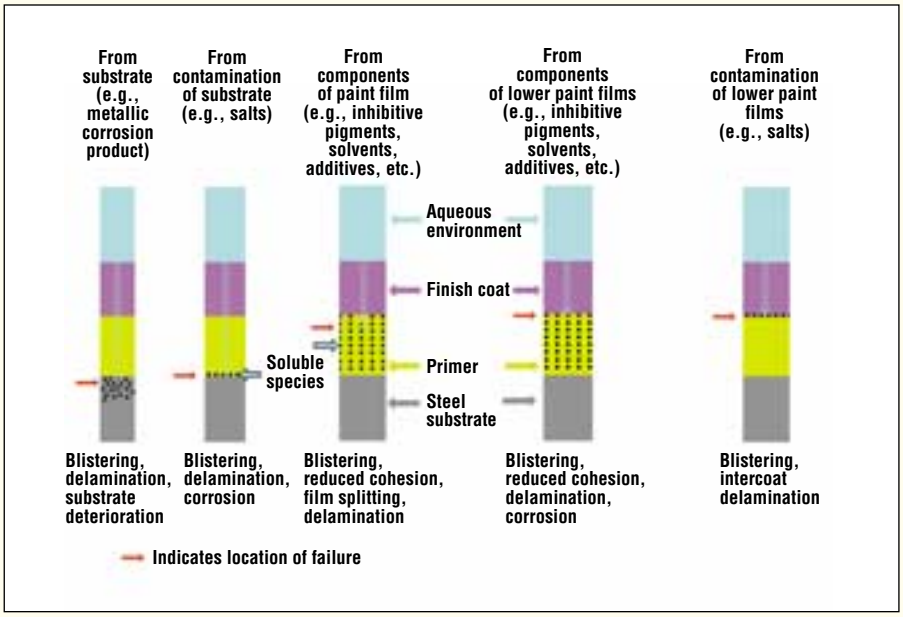


Fig. 3 - Sources, sites, and effects of osmotic blistering in coating films

Because metal is impervious to water, water cannot access the interface through the substrate (from beneath), as may occur on coated wood and concrete. It must always first go through the coating or at least progress along the interface from locally exposed sites such as pinholes, abrasions, and holidays. An important key to understanding

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the cause of blistering on metal can be found by isolating the driving forces that ensure the unidirectionality of water flow through the film to the substrate and there sustain the consequent accumulation.

Several recognized driving forces are associated with the production of blistering in coatings on metal by diverse mechanisms. These include osmotic gradients, producing blistering under fresh water conditions; electroendosmotic gradients, producing blistering in ionic solutions; and thermal gradients, producing the cold wall blistering often seen in humid environments. Cathodic blistering, produced by the generation of alkalinity at the cathode, is also associated with electrical gradients and is often driven by an externally impressed current. It is commonly a consequence of the application of high potential differences across coated substrates.

In this article, we will consider only osmotic blistering, which is thought to be the most prevalent type of failure. The article will discuss the mechanism of osmotic blistering, the factors contributing to osmotic blistering (including the nature and source of the solute), and the sources of osmotic gradients from the corrosion process, retained solvents, and non-carrier solvents. Corrosion caused by osmotic blistering will be characterized, and osmotic blistering at pinholes will be described.

The Mechanism of Osmotic Blistering

We noted in the November 1997 column that intact paint films are semi-permeable membranes, permeable to water, but impermeable to dissolved solids. This model is precisely that which accommodates osmotic blistering. The phenomenon (Fig. 1) depends on the presence of a water-soluble material at either the interface of the paint film with the substrate, or, in multi-coat systems, at some intermediate interface that is covered by another coat of paint. Often, the active material is an inorganic salt of some kind. In addition, the external face of the paint film (or system) must be in contact with an aqueous environment that is either free of or lower in dissolved material than the environment beneath the film.

Under such conditions, after water is absorbed by the film, it is subsequently transferred to the lower film interface (e.g., metal substrate). There it may come in contact with the soluble material on the substrate and leave the film to dissolve the material. Under fresh water conditions (distilled water or even high humidity), such sub-film dissolution

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creates a concentration gradient across the film, which here acts as a semi-permeable membrane. On the downstream side of the film where the solute is dissolved by water from the film, the solute concentration is much higher than is the solute concentration at the external (or upstream) face of the film. Under these conditions, water will be drawn through the film towards the concentrated solute, under osmotic pressure. This transfer of water occurs because the water pressure and salt concentrations on either side of the membrane attempt to equilibrate. The mechanism of osmotic blistering is illustrated in Fig. 2.

In quantitative studies of the phenomenon, van der Meek-Lerk and Heetjes[1] have shown that blisters initially grow fast, but the growth slows with time. Growth is still measurable after 160 days' immersion. Accompanying this growth is a progressive decrease in salt concentration within the blister, which increases the water concentration and progressively reduces the driving force of the growth.

External water that is relatively high in dissolved salts (e.g., salt water) will not favor the formation of osmotic gradients. In sea water, osmotic blistering is not normally a serious problem. However, the deionized water and condensate found in power generation facilities as well as potable water found in tanks and stand pipes may be particularly troubling. Rain water and high humidities are more generalized sources of water of low solute concentration, which can result in high osmotic pressure. But the duration of the "immersion" in simple exterior environments is normally too short to produce problems. However, persistent humidity and condensation in such environments has caused problems with films based on highly soluble corrosion inhibitors, such as zinc yellow.

The Nature and Sources of the Solute

Inorganic Salts

The nature of the solute below the semi-permeable membrane seems unimportant.[1] Osmotic blistering has been related not only to chlorides, sulfates, and other inorganic solubles often found on substrates, but also to organics such as sugar.

Notwithstanding this, blistering from aggressive depassivating salts such as chlorides and sulfates are of particular concern to the protective coatings engineer. These materials (unlike rust itself) readily accelerate further underfilm corrosion and blistering. Regarding corrosion, there is far more evidence of critical thresholds necessary to its initiation than there seems with respect to blistering. Estimates of permissible salt levels for underfilm rusting vary from 1.2 mg Cl^-/cm^2 and 10 mg $SO_4^=/cm^2$ (Igetoft[2]) to 500 mg Cl^-/m^2 (West[3]) and 50-100 mg $SO_4^=$ (Morcillo[4]). The subject is reviewed in detail by Alblas and van Londen.[5]

In the author's opinion, the search for permissible salt concentration thresholds at which corrosion will not occur is inevitably complicated by the variety of individual models possible. Not only is the relationship complicated by film thickness, but infinitely more so by film characteristics and the mechanism of corrosion control. (Zinc-based systems are far less vulnerable to salt contamination than are barrier systems, for example.) Inhibitor-based systems, relying on anodic passivation control, will be particularly vulnerable to these contaminations. Tolerable levels will depend upon the type and loadings of inhibitor used, pigment volume concentration (PVC)/critical pigment volume concentration (CPVC) ratio, pH of the mi-

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croenvironment beneath the coatings, and temperature. Other characteristics of the binder itself—permeability to water, oxygen, saponification resistance, and dielectric constant—will all have an effect. Thus, it would appear that permissible salt levels for underfilm corrosion resistance, if not good blistering resistance, will safely be the lowest level derived from the general experience, unless the thresholds for the particular system are known. Unfortunately, in many models, this position will inevitably lead to over-engineering.

For osmotic blistering alone, the type and molar concentration of solute seems most important to the size and morphology of the blister level. Morcillo et al[6] found that while ferrous sulfate concentrations produced a large number of fine blisters, sodium chloride induced fewer but larger blisters. The actual difference in the solute concentration on either side of the paint film membrane need not be large to support the continued growth of the blister. As is noted by van der Meek-Lerk and Heetjes, even trace amounts of hydrophilic surface contaminants may be sufficient to cause osmotic blistering.[1]

Blistering patterns reminiscent of fingerprints have betrayed untoward handling practices and the transfer of perspiration onto the steel by workers before painting. Most typically, it is, however, airborne salts such as chlorides derived from marine environments, bridge deicing salts, sulfates produced by acid rain and industrial effluent (SO_2, SO_3), and nitrogen oxides that cause frequent trouble. Abrasives (especially silica sand) have also been noted as a source of salt contamination[7], although SSPC Report 91-07 showed that the amount of salt transferred to substrates from abrasive was extremely low and did not produce blistering under conditions observed.[8] The number and variety of inorganic contaminants found on bridge structure surfaces is surprisingly large.[9]

Significantly, solubles accidentally or deliberately entrained in the coating itself may also cause difficulties. These materials may be readily transferred to the interface in water service. Highly soluble inhibitive pigments, such as chromates, molybdates, and borates within primer films may cause osmotic blistering either between coats or at the metal interface beneath the primer (Fig. 3). In 1991, the Pittsburgh Society for Paint Technology found that blistering could be related to the amount of water-extractable material in the paint film.[10]

Similarly, soluble species may be derived as a result of reaction or

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degradation of pigment or binder. Investigating severe blistering of an alkyd film in a mildly alkaline environment (pH 8.2), Bullet and Prosser attributed the phenomenon to a soluble residue derived from the hydrolysis of the binder.[11]

Elm[12] reports instances of osmotic blistering over zinc-rich primers that may become contaminated with water-soluble salts after priming. Redress may be difficult because of the porous nature of many zinc-rich films, especially in cases where the zinc film binder is non-soluble in solvents of the finish coat. Washing and rinsing the primer thoroughly with fresh water before topcoating may lessen if not eliminate the problem. Before recoating, the newly cleaned primer must be dry.

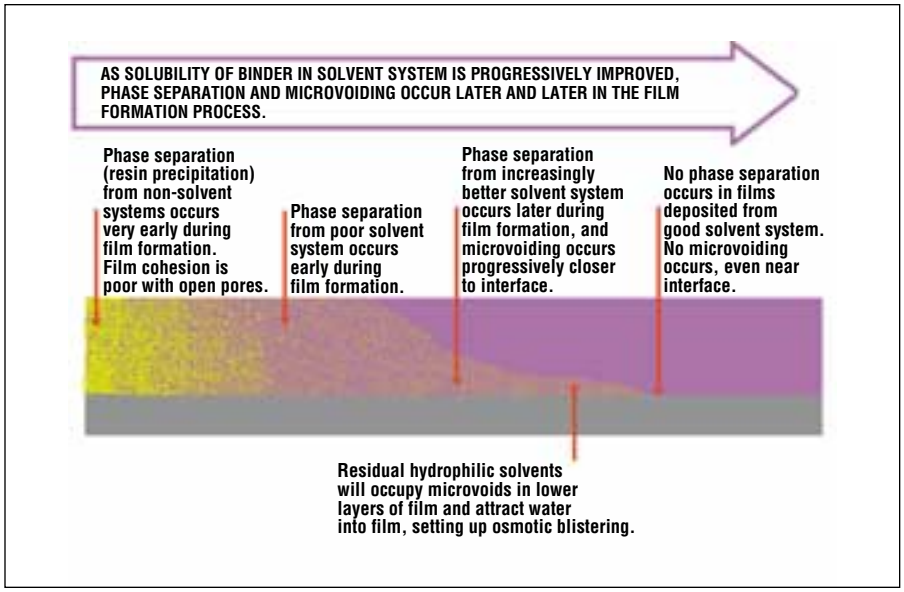


Fig. 4 - Phase separation, microvoiding, and solvent entrapment as a cause of osmotic blistering

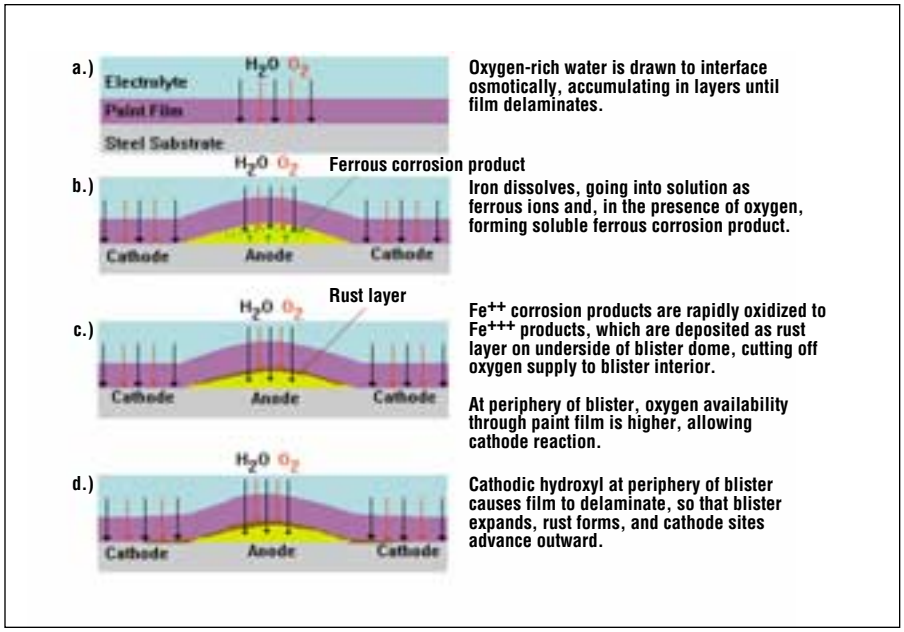


Fig. 5 - Corrosion process in osmotic blister

The Products of the Corrosion Reaction

Osmotic gradients may also arise directly from the corrosion process itself. Water and oxygen can directly access the metal at isolated sites of non-adherent film and crevices beneath the film where the paint failed to wet the substrate. Their corrosion products, which have some solubility in water, may cause trouble. An example of these corrosion products is $Fe(OH)_2$. These too may initiate osmosis, especially where oxygen concentrations are low enough to delay the secondary oxidation process to the more insoluble ferric (Fe(III)) compounds. Where chlorides and sulfates are simultaneously present, the corrosion products (ferrous chloride hydrate and ferrous hydroxy sulfate) are even more soluble in water. With certain vulnerable ester-based binders (e.g., oil alkyds), the high pH generated at the cathode may hydrolyze the polymer. This reaction not only loosens the adhesion of the coating at the periphery of a blister (so enlarging it), but also simultaneously produces soluble degradation products such as alkali metal soaps, which also encourage osmotic blistering.[11]

Retained Solvents

Osmotic blistering can also be caused by the retention of hydrophilic solvents and diluents within the film (most often high boiling alcohols, glycol ethers, and esters). Under suitable conditions, these solvents may remain in the film for months. Many of these solvents are highly miscible with water and residual quantities of these materials will draw water through the film osmotically, similar to the effects of soluble salts. Blistering similar in appearance to blisters caused by subfilm salts will result from solvent retention. The reasons for such discrete blister formation in films having supposedly uniform solvent distribution (as opposed to the

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wholesale delamination of films so affected) is explained by Funke.[13]

Funke has investigated the morphological structure of paint films deposited from mixtures of solvents and diluents.[13,14] This research has shown that the onset of incompatibility and phase separation in films containing low boiling solvents and high boiling diluents will depend upon 3 factors:

- the type and ratio of the solvents and the diluents;
- the application temperature; and
- the glass transition temperature (T_g) of the binder.

The morphological structure of the film depends on when incompatibility sets in during conversion of the film from liquid to solid. In well-formulated systems, films pass into the glassy phase without any phase separation at all, and clear, continuous films result. In systems with higher concentrations of high boiling diluents, incompatibility and phase separation set in more rapidly, potentially resulting in various anomalous morphologies. In extreme cases, the development of incompatibility early in the film formation process will produce precipitation of the binder, resulting in a non-continuous film. If phase separation occurs only slightly before the onset of gelation, the film may be coherent, but it will tend to contain large, open pores. Phase separation occurring subsequent to gelation will result in a closed, continuous surface layer covering a microvoided interior. As phase separation occurs nearer and nearer to the time that the film passes into the T_g state, the film will be progressively freer of microvoids.

Significant to our discussion of osmotic blisters is the fact that the reduced microvoiding, noted as phase separation that occurs later and later during film formation (or as the solvent system progressively improves), does not uniformly disappear. Rather, it shifts downwards, occurring at deeper layers of the film nearer to the interface, at which location it is most likely to be found. Hydrophilic diluents and marginal solvents are found primarily within these microvoided areas close to the interface (Fig. 4).

Under conditions favoring osmosis, water diffuses through the film towards these microcellular inclusions adjacent to the interface. The rate of water diffusion under osmotic pressure differentials is much greater than is any tendency of the entrapped solvents and diluents to desorb water from the film. Thus, water accumulation is progressive and results in a blister pattern resembling the microstructure itself. Funke[14] used vinyl lacquers for his investigation. In practical protective coating systems, the formulation practices (low boiling solvent, high boiling diluents) he employed are the exception rather than the rule. However, with many thermosets, Funke's arguments become more valid. Their molecular weight increases and solubility profiles change as a result of some conversion process (chemical cure and oxidation). Some degree of phase separation may even occur with truer solvent systems as the cure progresses and solvency decreases.

These phenomena are aggravated by increasing film thickness, where the solvent (and non-solvent) retention is greater and the microcellular structure more entrenched. The blisters are often found to contain water and hydrophilic solvent (diluent), although corrosion may not immediately initiate.

If the film is post baked at temperatures well above the T_g before exposure, the offending solvent may be released, and the osmotic pressures will not develop.

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Osmotic Blistering by Non-carrier Solvents from the Service Environment

Related effects may occur from hydrophilic solvent imbibition in service. Coatings on the interior cargo spaces of tankers handling methanol have been known to develop severe blisters, but only after the tanks were discharged and refilled with water. This blistering was not seen where the same coatings were continuously exposed to either methanol or water alone.[15] Methanol uptake by most coating films is likely. (The molecule is small and is widely used for just this purpose in paint removers.) The retention of water-miscible solvent (e.g., methanol) within the film after the tanks are emptied and then refilled with water will pull water more readily into the film, osmotically producing the observed blistering in a manner similar to that noted above by Funke.[12]

In some cases, solvent-induced osmotic blistering may be quite unexpected. It has become common for epoxy formulators in these days of low VOC coatings to extend pot lives of amine-cured epoxy systems with ketones. Ketone solvents form latent ketimines with amine curing agents, which effectively tie up the amine until after the coating is applied. Upon application, water from the atmosphere reverses the reaction, releasing the amine as the ketone evaporates. The rate of dissociation will probably depend upon the type of ketone used, the relative humidity and temperature of application, and other factors such as pigmentation. Platey metallic pigments, which reduce the rate of moisture ingress into the wet film and ketone release out of the film, will prolong the reaction in the lower layers of the film. So too will high film thicknesses, which may also cause heterogeneous cure with the upper surfaces curing over the uncured or the lesser cured lower layers.

Very polar solvents (e.g., ketones) associate quite readily with water. Some, such as methyl ethyl ketone (often used in this type of coating), are in fact water miscible. Should incompletely cured films of this type be placed in immersion service before complete dissociation of the ketimine (or release of the methyl ethyl ketone), osmotic gradients can be set up readily. Water penetrating the heterogeneously cured film may release ketone in the lower layers and associate with that ketone, producing osmotic blisters. While still rare, the phenomenon is seen more often with coatings developed since the early 1980s, when ketimine cross-linking agents became more popular. The phenomenon has been described by Tator.[16]

Similar phenomena are also possible with condensation cures in which alcohols are released. One example is incompletely cured ethyl silicate zincs after recoating and initiation of immersion service. Here, however, other failure mechanisms may predominate, such as pure stress effects leading to later splitting of the zinc film.

Corrosion from Osmotic Blistering

Corrosion in the local environment beneath an osmotically formed blister does not necessarily occur immediately, especially if the liquid within the blister does not contain depassivating salts. Eventually, when corrosion does initiate, the underside of the dome of the blister becomes covered in a greenish-black corrosion product, which may itself have osmotic consequences. As Funke[13] notes, corrosion is, however, a sequential process unconnected with initial blister formation. In this case, corrosion of the metal beneath the

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blister probably depends upon oxygen permeability of the coating. Corrosion proceeds as shown in Fig. 5.

If the blistering phenomenon results from soluble inhibitive moieties (chromates and borates) included within the paint film as pigments, then the metal beneath the blister may remain bright without forming corrosion products for several months. This condition can occur even under accelerated high humidity test conditions designed to accelerate blistering failure.

Once the blister is formed, corrosion will occur by general cell activity between localized cathodes and anodes on the metal beneath the blister. It will be largely controlled by oxygen permeability through the film. Where oxygen permeability is negligible, corrosion may be delayed indefinitely. The onset of corrosion may also be delayed if the external environment is oxygen deficient.

Given the transmission of oxygen and water to the interface, osmotic blistering may well occur in the absence of externally derived salts or other hydrophilic materials, as a result of the corrosion process. This scenario requires the pre-existence of some site of localized deadhesion where water may first accumulate. Corrosion rates would initially be low because of the high resistance inhibition provided by the non-ionic water solution. However, the formation of soluble corrosion products within the blister would set up osmotic gradients under favorable conditions, leading to increased osmotically induced blistering.

Thus, osmotic blistering in deoxygenated, deionized water systems, such as are used in the nuclear power industry, does not produce corrosion within the blister. In nuclear power generation facilities, the vapor phase of the taurus (the cooling water vessel beneath the primary containment areas) is flooded with nitrogen gas. The nitrogen is thought to maintain bright, uncorroded steel beneath blisters that may form under the coating in immersed areas. In this case, the blister growth is stabilized (as the osmotic pressure involved is balanced by the hydrostatic pressure of the head of water).

It may be prudent to ignore the blistering and leave the system in place without repair. In Japan where the taurus is never drained, coatings have provided good service for 18 years or more in spite of such blistering. In the U.S., where similar vessels are drained for cleaning and inspection every 2 years (exposing the interior of the blister to oxygen during downtime), the blisters reveal underfilm corrosion. This, together

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with associated cracking and deadhesive propagation, reduces the service life of the coatings to approximately 8 years.[17] (Absorbed water will plasticize the film under wet conditions, and the wet, distensible film may easily retain the blister deformation. As the water is desorbed from the coating during downtime, the film becomes less plastic. Hygroscopic tensile stresses arising from the drying process may exceed the tensile strength of the film, resulting in a cracking failure.)

In more usual circumstances, corrosion will follow the onset of osmotic blistering more rapidly, although the 2 phenomena remain sequential rather than mechanistically related. As noted above, the rate of corrosion depends on the rate of oxygen permeability through the film and into the blister. Oxygen is consumed at the cathode site within the blister in the formation of hydroxyl ions and cathodic depolarization. It will also react with the initially produced ferrous ions to oxidize them to the ferric state. This latter reaction soon predominates. Ferrous ions accumulate within the blister, consuming the available oxygen immediately as it enters the blister cavity. The ferric ions coat the underside of the blister dome with a precipitated layer of greenish-black corrosion product (probably ferroso-ferric hydroxides and magnetite, Fe_3O_4). This layer further restricts access of oxygen to the interior of the actual blister cavity, depriving the underside metal of fuel for the cathode reaction. This area (beneath the blister dome) thus becomes uniformly polarized anodically. The cathode sites shift to the periphery of the blister where the film is intact but in contact with water (laterally from the blister) and oxygen. Oxygen gains access through the film, which is still adherent and without the seal of corrosion product. The formation of cathodic hydroxyls at the periphery of the blister creates an alkaline condition under which adhesion may be lost; thus, for certain coatings, the area of the blister expands. The diffusion of ferrous ions to the newly formed cathodic sites is followed by their precipitation onto the cathodic steel around the periphery of the blister as ferric compounds. If at this point the film is stripped from the metal, a pattern of annular rings of greenish-black rust is noted, while the area of the steel immediately beneath the blister dome is brighter (Figs. 1 and 6). The undersides of the blister dome are similarly greenish-black in color (Fig. 7).

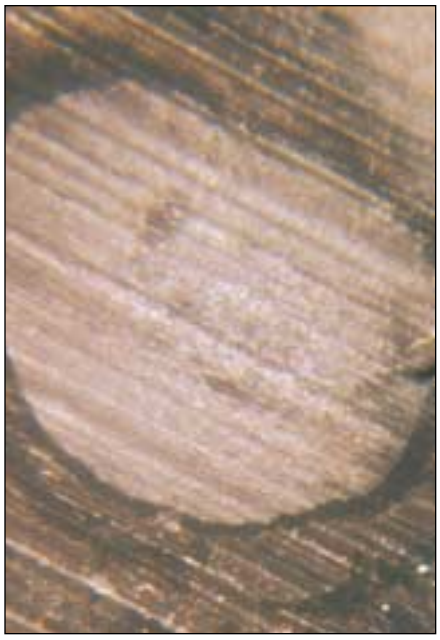


Fig. 6 - Photomicrograph of steel surface beneath osmotically blistered coating. Note steel surface beneath dome of blister is bright and surrounded by circular areas of green-black corrosion product.



Fig. 7 - Underfilm condition after osmotic blister formation—showing the deposit of corrosion product underneath blister domes (the other side of the interface shown in Fig. 6, from which film delaminated)

Osmotic Blistering at Pinholes

Osmotic blistering is also possible at discontinuities in the film, as long as the defect area is not too large (pinholes and pores rather than abrasions, gouges, and large holidays). In this case, however, blistering and corrosion phenomena are more interdependent. The condition is again described by Funke.[13] He notes that in all cases the onset of blistering is preceded by the appearance of corrosion at the pinhole, which eventually becomes the peak of the blister dome. The defective, semi-transparent membrane caused by the blister is repaired by a plug of corrosion product (hydrated iron oxide), which forms at the bottom of the pinhole channel. Under the sealed conditions, blister formation by osmosis can now occur. The

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soluble species is soluble ferrous compounds. Corrosion products beneath the plug sites set up an osmotic gradient across the now repaired film. Again, the growing blister becomes oxygen depleted because the ferrous to ferric oxidation process consumes the available oxygen as soon as the oxygen enters the blister. Anodic polarization of the base of the blister site and the shift in cathodes to the blister peripheries follow as noted above.

Conclusion

Next month's article will review non-osmotically driven blistering of coatings on metal. ❐

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