Non-Osmotically-Induced Blistering Phenomena on Metal

Last month, we discussed one of the most common types of blistering of paint films on metal—osmotic blistering. Now we will consider other forms of blistering, including electroendosmosis, cathodic blistering, cathodic disbondment, and compressive stress-related blistering.

Electroendosmosis

In the 1940s, Kittleberger and Elm noted that blisters on panels immersed in sea water occurred only after areas of the panels had begun to corrode, either because they had been incompletely coated, or because the coatings were breaking down at cuts and abrasions. Totally protected panels showed no blistering. The researchers later confirmed that the blistering of these panels was electroendosmotic in origin, caused by the establishment of a naturally occurring electrical gradient across the film.[1] During electroendosmosis, or electro-osmosis, water is forced through the paint film by an electrical potential gradient. The flow is toward the electrode that has the same charge as that acquired by the immersed film. (This may not be the same with all films or in all liquids.) Most films acquire a negative charge in water, and the metal substrate around the corroding area is cathodic and therefore rich in electrons. Thus, the water is naturally drawn through the film, so that blisters will occur around the corroding site.

The 2 researchers measured the amounts of water absorbed by oil paint films on steel immersed in salt water and the extent of associated blister formation. They found that levels were much greater when the panels were electrically coupled to freely corroding (anode) panels than when the panels were uncoupled. It was shown that electroendosmotic influences accounted for between 95 and 99 percent of all water absorbed by the coatings involved, and that under these conditions, osmotic effects were minimal. Pigmentation was also found to be important to the process. Oil paints pigmented with red lead and zinc chromate showed much lower levels of water absorption and blistering than did systems pigmented with chrome yellow and red iron oxide over the same immersion period. In less than 11 days, the latter systems delaminated entirely. Because both binder system and pigment volume concentration (PVC) were normalized in all systems, it was believed that electroendosmotic effects and electrolytic resistances of the film were associated with pigmentation, not the binder.

Fig. 1 - Electroendosmotic blistering around a cut scribe and discrete corroding points.
Figures courtesy of the author

Although the phenomenon is primarily seen under electrolytic immersion (i.e., sea water immersion), it is often noted on scribed panels in salt spray testing (Fig. 1).

Some authors have concluded that once corrosion begins, electroendosmotic blistering may be a primary driving or accelerating force for blistering.[1,2,3] This seems to be the case for the oil paints used by Kittelberger and Elm, but the justification of such conclusions is generally open to some dispute. Funke, for example, believes that this type of driving force is much less universal than is the osmotic force.[4] More work is needed to discover the importance of electroendosmosis in blistering.

Cathodic Blistering

As discussed in the December 1997 column, alkali is produced at the cathode under basic and neutral conditions as part of the corrosion process. This reaction is expressed as $O_2 + 2H_2O + 4e^- = 4(OH^-)$.

Cathodic blistering is caused by this electrochemical reduction of oxygen beneath intact (and sometimes defective) coatings. Water,

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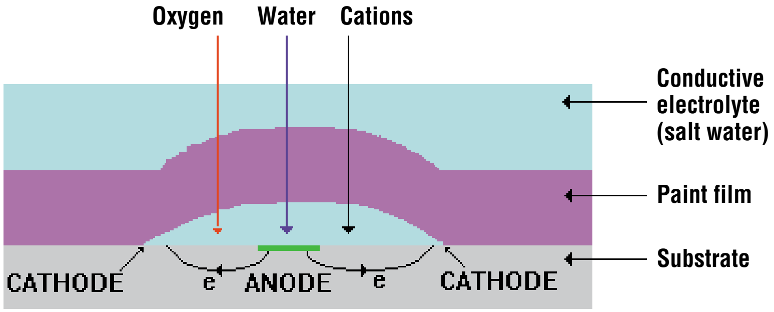

At the cathode, oxygen reduction [$O_2 + 2H_2O + 4e^- = 4(OH^-)$] creates an increasingly alkaline condition.

Alkali attacks metal oxide and paint film as well as any conversion coating (e.g., zinc phosphate), producing delamination and expansion of the blister.

Where film is defective and corrosion is occurring at a nearby site, the blister may be entirely cathodic, with electrons being supplied from the nearby corroding site.

Fig. 2 - Cathodic blistering

oxygen, and alkali metal cations (e.g., sodium cations) diffuse through the coating to cathodic sites to produce strongly alkaline solutions. Anodic sites may be located at the center of the blister or in defective films at nearby corroding sites (Fig. 2). As the reaction is localized beneath the coating film, the hydroxyl ions are trapped by the semipermeable film at the site of adhesion loss (the incipient blister). There, ionic accumulation equates with increasing pH.

Although the actual mechanism of film delamination from the coated cathode is only partially understood, it seems likely that the hydroxyl ions may attack the coating binder, the metal oxide surface, or the bond between the two. A loss of adhesion involving the alkaline hydrolysis of coating films based on ester and possibly amide (including urethane) linkages is reasonable. Or the alkali may dissolve phosphate conversion coatings on pretreated steel, leading to undercutting of the coating system.

The saponification and solubilization of oil paint films around the scribed area of salt spray panels is common. Carboxylated residues

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from this type of attack have been identified beneath cathodic blisters in melamine cross-linked epoxy ester and polyester films.[5] Byrnes examined infrared spectra of vinyl chloroacetate linings after exposure to excessive cathodic protection potential. The data show depression of the carboxylic ester peaks and increased hydroxyl functionality in the area of the film immediately adjacent to the steel.[6] This indicates breakdown of the ester to the relevant alcohol and (presumably) acid.

As discussed in our February column, alkaline hydrolysis can result in propagation of adhesion loss by film undercutting around the peripheries of simple osmotic blisters. However, there are also reports of alkali attack on the metal oxide surface[7], with pH values up to 14 being noted at cathodic delamination sites.[8] These values are basic enough to solubilize ferric ions and disrupt the metal oxide surface.

The effect of alkali on the increased rate and magnitude of water take-up by polymers was noted in the September 1997 column. Thornton et al. concluded that the greater degree of water saturation of the film resulting from increased hydroxyl ion concentration may exacerbate de-adhesion.[9] Then, mechanical distortion of the film (leading to rupture of interfacial bonds) and the pooling of water at the interface are likely to propagate adhesive loss.

Cathodic Disbondment

Where steel is to be buried (e.g., underground pipelines and tanks) or immersed in water, it is normal for the first line of defense against corrosion to be cathodic protection via impressed currents. The process essentially protects the steel surface by connecting the structure electrically to a permanent anode (or anode array). An impressed current is directed between the steel and anode in such a direction so that no current is discharged from the steel to the environment (soil, backfill, or water). Thus, the steel is maintained as the cathode of a huge electrochemical cell and is thereby protected. Cathodic protection by impressed current systems is detailed by several authors.[10] The technique is highly effective, but large steel areas require large amounts of current to maintain flow in the right direction. To minimize the consumption of electricity, the size of the steel surface exposed to the environment is usually diminished by coating it (thus reducing the area requiring protection to small areas at bare spots).

In practice, the electrical potential of the coated steel should be slightly more negative than -0.8 volts (with reference to a copper/copper sulfate reference electrode), usually about -0.85 volts. This effectively maintains protection at remote locations in the presence of holidays, locally uncoated areas, and steel protrusions, where the current may drain to earth.

However, the applied voltage cannot be too high, for high over-voltage potentials (more negative than about -1.1 volts with reference to the same electrode) may produce blistering and delamination of the coating in areas around the same bare spots and defects.[6,11,12] Such delamination increases the areas of bare steel on the structure and therefore the current requirement and cost needed to maintain cathodic protection.

Cathodic delamination in underwater systems (such as ships' hulls), which employ sacrificial zinc or aluminum anodes with fixed potential differences with respect to the steel, are not as liable to produce the same degree of over-voltage potential as are impressed current systems. However, cathodic disbondment is not an unusual coating failure under these conditions.

The voltage of the structure with reference to a copper/copper sulfate reference electrode must be constantly monitored and adjusted automatically or manually to changing environmental conditions if the non-corroding condition is to be safely maintained without developing an over-voltage. This may be particularly important where the vessel may move through waters having different salinities, and, therefore, different resistivities. The applied potential must be decreased as the vessel moves into water of lower resistivity (higher salinity). In high resistance electrolytes, the protected area may become quite limited unless the applied potential is increased. The increased potential may severely endanger the coating system in the immediate areas of the anode. Because of this risk, the anodes are often shielded with special devices to withstand the cathodic conditions near the anode.[11]

Impressed current systems are also widely used for protection under fresh water. Again, the same over-voltage limitations apply. These systems are often used along with suitable coating systems (usually epoxies) to protect potable water tank interiors. Failures occur, however, in many instances because the systems are improperly installed, misused, or improperly maintained. Anodes are left unconnected or not replaced, or systems are not switched on. The installation must be made and maintained by competent professionals.

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For example, it is important that the reference electrode be properly placed in the same general area as the anode array. Dubcak reports an instance of severe cathodic blistering in a tank where voltage readings at the cathodic protection controller box were no higher than -0.9 mV.[13] In this case, the reference electrode was electrically shielded by its installation in a well, separate from the anodes. High current readings (4.0 mA) tipped the analyst that something was wrong, and over-voltage measured at anodes well removed (shielded) from the reference electrode was found to be as high as -2.7 mV. When the reference electrode was raised into the belly of the tank, closer to the anode array, current demand dropped markedly, and potential readings for all anodes dropped to near -1.0 mV. When the tank was repaired, the new alignment of the reference electrode was standardized. There has been no further blistering.

As Leidheiser states, good protection against cathodic disbondment (in systems with cathodic protection and in those without) requires that the interfacial region be highly resistant to alkali.[14] Optimizing the alkali resistance of the coating film (eliminating hydrolyzible groups such as esters, amides, urethanes, and urea linkages), perfecting wet adhesion, improving dielectric strength, and minimizing film transport properties seem to be avenues toward this goal. At a high enough potential (more negative than -1.0 volts vs a standard calomel electrode), hydrogen formation is also possible, i.e., $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$. The evolution of hydrogen gas may itself force the film from the steel.

Thermal Gradient-Induced Blistering (Cold Wall Effect)

Blisters result from water condensation produced by thermal gradients across coatings.[15] This effect is often seen on the coated interior surfaces of cold tanks containing warm water. Hendry reports examples of the phenomenon in the Middle East where blisters appeared on the interior walls of tanks containing warm, distilled or deionized water.[16] Apparently, water is absorbed into the coating at the warm side of the paint film (away from the substrate). Water condenses at the interface with the metal, where the temperature and therefore the permeability of the film are low enough to prevent the same rate of movement back into the film towards the higher temperature interface. (Thermodynamic activity of the water/paint film model will be greater at the warm face of the coating than at the cold face next to the metal.) Presumably, water must condense at a point of weakened adhesion (perhaps a point of contamination or stress center) and there accumulate.


Fig. 3 - Blistering on tank exterior induced by thermal gradients. (Inside fluid was cold; outside environment was warm and humid.)

Tator reports studies indicating coatings with low permeability are more resistant to cold wall effects than more permeable ones.[17] Cold wall effects occur most often at the interface of the metal and the coating. However, failure may also occur at a primer/finish coat interface.

Cold wall effects may also occur on non-immersed exterior coatings of tanks containing cold water or fuel in humid environments.[18] The propensity of the phenomenon to show up on storage tanks is probably related to the heat sink properties of the large body of liquid within the tank. Cold wall blisters are often very large. The author has noted large blisters 10 in. (25 cm) in diameter on the coated exterior walls of fuel storage tanks containing cold fuel in summer (Fig. 3). When these large blisters were punctured, copious amounts of water flowed out. This occurred in New York State on a dry day, following a relatively humid spell of weather. Delamination occurred at the primer/finish interface but not at the metal itself. Obviously, this interface was less secure than was that of the thin film of primer to the metal. It seems likely that osmotic effects, probably related to inhibitive pigments within the primer, also played a role in this failure. It is possible that during periods of high humidity, the film takes up water vapor, which condenses against the cold metal interface on the exterior of the tank.[19] Subsequently during the heat of day, the condensed water may expand and attempt to evaporate, developing high pressures over a relatively short time on the underside of the impermeable film, which may lead to the physical expansion of the blister.

Cold wall phenomena are intensified by the relative thermal conduction properties of the metal (excellent) and the coating (poor). Small temperature differentials may produce cold wall blistering. It is most often eliminated by proper tank or pipe insulation.

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Fig. 4 - Steel exposed by thermal stress-induced blistering. (Note circular patterns relating to stepwise progression of failure.)

Discussing the same phenomenon on the coated interior walls of tubes, Schwenk found that the "incubation time for the onset of blistering" increased as the temperature gradient between the warm water on the inside of the pipe and the external environment was reduced, either by reducing the water temperature within the pipe or (presumably) by increasing the temperature of the exterior environment.[20] The danger of peeling could also be reduced by using a thicker coating in the tube.

Corrosion is not expected to immediately follow the onset of cold water blistering, and will largely depend on the rate of oxygen transmission through the film.

Several humidity tests (e.g., ASTM D 4585, Standard Practice for Testing Water Resistance of Coatings Using Controlled Condensation, and ASTM C 868, Standard Test Method for Chemical Resistance of Protective Linings) are based on blistering induced by thermal gradients.

Blistering and Delamination of Films from Compressive Stress

In 1964, Brundt postulated that blistering could result from the paint film's response to compressive stress in the absence of osmosis or any other driving force.[21] Where the adhesive strength of the coating was unable to accommodate the swelling of the film from hygroscopic stress, thermal stress, or other factors, the film would delaminate as a blister. This type of failure looks different than other forms of blistering. Often in thermosetting systems such as epoxies, urethanes, polyesters, and older alkyds, de-adhesion generally occurs in large, irregular flakes and sheets rather than as discrete hemispherical blisters. The interiors of these stress-induced "blisters" are quite dry, and the domes are less defined. The delaminating film segments have a typical convexity towards the coating/air interface (concave to the substrate), which betrays response to compressive stress. Usually, such delaminations can be detected before any actual flaking occurs; an audible response to a tapping of the areas with a finger indicates some intra-system cavity. Failure may sometimes progress outwards from a central point of initiation, leaving a series of concentric cracks (Fig. 4).

In thermoplastic systems (especially where the ambient temperature is above the glass transition temperature ratio), the films are often too elastic to blister. However, if stretched beyond their yield point, the films may exhibit wrinkling on removal of the stress (cooling or drying out). There may be some adhesive recovery at this point, although if adhesion is very poor, the film may be removed in large, flexible sheets of paint.

Blisters having discrete, localized formation (that may be related to compressive stress alone) are uncommon.[4] However, they are possible. Discrete, dry blister formations in a marginally adherent latex paint system over coil-coated aluminum stock have been noted by the author as a response to the application of heat alone. On cooling, these blisters disappeared.

Leidheiser studied the response of an epoxy film to swelling stresses produced by exposure to 0.1M H_2SO_4 at 60 C (140 F).[22] He observed that blister formation was related to adhesion. When the substrate was abraded, the film expanded in a single large blister; when the substrate was blast cleaned (presumably resulting in greater film adhesion), several much smaller blisters were noted. The effect is often seen in both acid and solvent resistance testing.

Martin et al. propose a non-osmotic model for defect-controlled cathodic disbondment that relies on a sort of stress corrosion cracking process. In the model, the simultaneous effects of in-plane compressive stress and alkaline attack contribute to de-adhesion.[23]

Other Blistering Phenomena

Other blistering phenomena on steel are not as conveniently classified, although one or more of the above-mentioned mechanisms (including osmosis) may be involved. An example of such is the Dia Phenomenon discussed by Van Laar.[24] In this effect, steel coated with a paint system predisposed to blistering in fresh water was observed to bear blister-free areas on coated surfaces corresponding to bare (freely corroding) areas on the back of the same panel. Simultaneously, corrosion was noted beneath the non-blistered areas. Areas of the same panel coated on both sides exhibited heavy, water-filled blisters. The effect was originally ascribed to the diffusion of atomic hydrogen from

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the freely corroding back areas through the steel to the coated side of the panel, where on reaction with oxygen, it causes the establishment of oxygen concentration cells. While there seem to be several problems with this interpretation, the phenomenon deserves more investigation.

Similar front side/back side effects were noted by Hare when investigating the corrosion resistance of latex paint on steel.[25] The intensity of corrosion on the front face of the coated panel was much more intense when both sides of the panel were completely coated than when the back face of a panel bearing the same system was allowed to corrode freely. In this case, the phenomenon was attributed to protective galvanic effects. These effects were provided by the freely corroding bare anode side of the panel to the coated side of the panel (cathode). They were not present on the totally coated panel, which corroded by local cell action.

Blister Analysis

Much can be revealed about the cause of blistering from a study of the blister interior, often found to contain fluid. When a blister breaks, the fluid may be ejected with some force, indicating the presence of a pressure gradient. The fluid may be extracted with a syringe and examined for pH and inorganic or organic residues. Solvents and carboxylic acid residues may be identified by gas chromatography. Often, the film will reveal entrapped solvent by a definite odor that is detectable as the blister is opened. The appearance of the steel surface is also telling. The presence or absence of visible scarification (and, therefore, maximized or compromised adhesion) and the condition of the steel give clues about the cause of blistering. Bright steel may indicate the presence of active inhibitors from the primers. (Chromate may give yellow fluids.) Uncorroded steel may also indicate cathodic blistering, which may be confirmed by the presence of a fluid of high pH. Blister formation between coats may contain soluble residues derived from a primer or intermediate coat. These residues may be detected by atomic absorption or wet chemical analysis; diphenyl carbohydrazide may be an indicator for hexavalent chromium compounds, for example, while dithizone may be an indicator for zinc cations.

Oils, grease, perspiration, and similar contaminants can lead to coating failure. Specifically patterned or irregular delamination is more likely than discrete, symmetrical blistering. The presence of moisture and dew during recoating may also cause problems;

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these problems are more difficult to determine on recoats than on the steel (which may exhibit corrosion). Moisture contamination is sometimes made evident by other problems: cissing and crawling of the finish, and bubbling and foaming with urethanes. Many of the more polar systems today (especially the primers) may partially displace or take up water.

Blisters may contain no water. In this case, the possibility of other forms of distress should be investigated, such as the generation of gases by the coating. Bubbling induced by entrapped gas (CO_2 in urethane films) will result in dry blisters, although the blister will form within the distressed film rather than at the interface.

Blistering and Delamination

Blister formation is preceded by loss of adhesion, which was identified as

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a necessary precursor to corrosion by Funke.[26] Initiation of adhesion loss may be difficult to identify before blisters actually become visible. Various techniques that seem promising in identifying the aspect of de-adhesion have been used to study both phenomena. These methods include the crossover point technique in the water transmission of supported and unsupported films developed by Funke[27]; and the infrared thermography techniques of McKnight and Martin.[28] Jin et al. injected a fluid between the coating and the substrate using a hydraulic pump.[29]

Using tests of this type, it is not only possible to quantitatively measure the adhesion of coated specimens to steel as immersion (or salt spray testing) progresses, but also to identify recovery of adhesion as the systems dry out after testing.

Other investigations are needed to add to our understanding of blistering and delamination.

Conclusion

This concludes our discussion of blister formation in coating films on metal in aqueous environments. The next several columns will focus on improving the understanding of the mechanisms by which coatings impede corrosion. ❑

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