

## **CORROSION MECHANISMS OF PAINTED METAL**

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### **ABSTRACT**

The corrosion mechanisms of painted metal will be discussed. Key topics covered include: (a) the electrochemical aspects of corrosion, including cathodic and anodic reactions; (b) the electromotive series; (c) the forms of corrosion that are relevant to painted metal, namely galvanic corrosion, crevice corrosion, and filiform corrosion; (d) mechanistic characterization of paint blistering, and cathodic and anodic delamination of paint films; and (e) the key points to control corrosion of painted metals. Specific examples of how innovative nanocomposite coatings can effectively counteract these corrosion mechanisms to improve corrosion resistance of various metallic substrates will also be presented.

Keywords: nanocomposite, pretreatment, corrosion, painted metal, electrochemical corrosion, electromotive series, galvanic corrosion, crevice corrosion, filiform corrosion, cathodic delamination, anodic delamination

### **INTRODUCTION**

The purpose of this document is to provide an introduction to the fundamentals of corrosion and its relevance to painted metal. The intent is to provide a general background on the subject that may be useful to both technical and non-technical personnel who are not familiar with corrosion technology. It is not intended to be an exhaustive dissertation on the subject.

A paint coating imparts two important functions to the underlying substrate:

- The aesthetic function gives the substrate a good appearance.
- The protective function protects the substrate from mechanical and chemical damage.

However, due to routine wear and tear, surface scratches and other defects are generated in the paint film and micro-cracks develop. These micro-cracks eventually lead to macroscopic corrosion damage, which results in the coating losing its aesthetic and protective functions.

Corrosion is a ubiquitous and on-going problem for the Department of Defense and the United States in general. It causes tens of millions of dollars of damage annually and compromises the safety, environmental, and appearance characteristics of the affected structures.

## THE CORROSION BATTLE

The battle of corrosion is a constant fight because of the curse of all corrosion engineers and scientists – thermodynamics! The Third Law of Thermodynamics states, in simplified terms, that the naturally occurring state of matter is its lowest energy state, similar to humans on weekends. Metals ordinarily exist naturally as oxides (e.g. iron oxide, aluminum oxide, etc.) because oxides represent their lowest energy state. However, oxides are mined from the ground, and they are subjected to various unnatural acts – such as refining, casting, rolling, and forming into a myriad of different shapes. These metals are now in an “activated” state, and do not want to stay there. They want to revert back to their naturally occurring state – oxides, or rust in the case of steel (Figure 1).

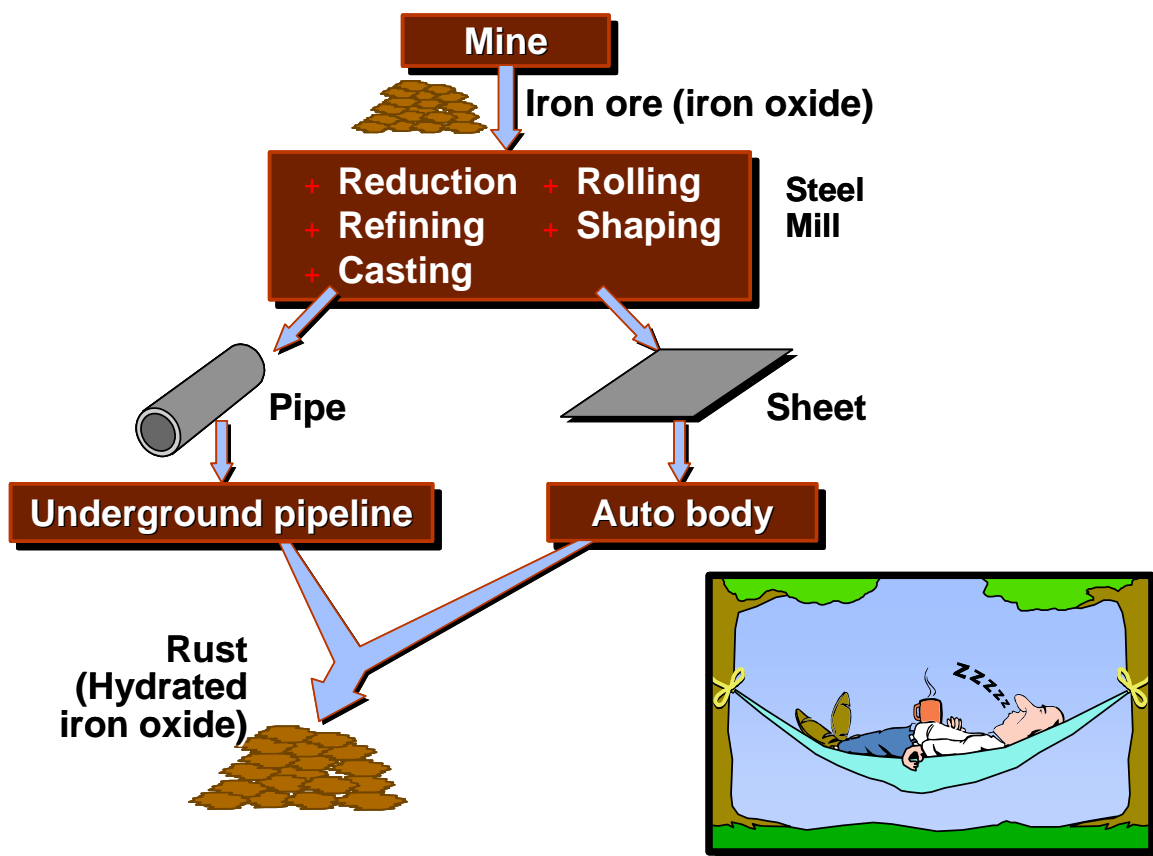


Figure 1 – Metals Want To Stay in Their Lowest Energy State as Oxides

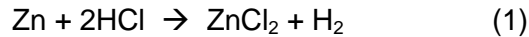
So that's what corrosion engineers do on a regular basis – fight the Battle of Corrosion to maintain the metal in its processed state and prevent regression to its natural oxide (corroded) state. One of the many ways this is accomplished is by applying metallic and paint coatings.

## ELECTROCHEMICAL ASPECTS OF CORROSION

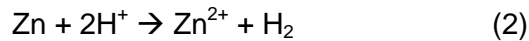
Corrosion can generally be classified as “wet” or “dry”. Wet corrosion, as the name implies, occurs when a liquid is present. This is the type of corrosion that is almost always associated with the corrosion of painted metal. This paper will discuss wet corrosion only.

Dry corrosion occurs in the absence of a liquid phase. Vapors and gases are usually the corrodents. Dry corrosion is most often associated with high temperatures (e.g., attack of metal by furnace gases). Dry corrosion will not be covered in this paper.

Wet corrosion is an electrochemical process. The electrochemical nature of corrosion can be illustrated by the attack of zinc in hydrochloric acid. When zinc is placed in dilute hydrochloric acid, a vigorous reaction occurs; hydrogen gas is evolved and the zinc dissolves, forming a solution of zinc chloride. The reaction is:



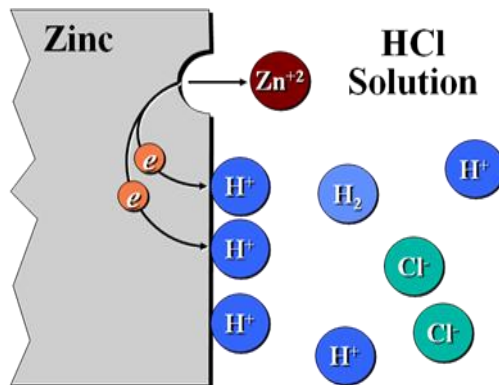
The chloride ion is not involved in the reaction; therefore, this equation can be written in the simplified form:



Thus, zinc reacts with the hydrogen ions of the acid solution to form zinc ions and hydrogen gas. Examining the above equation, it can be seen that during the reaction, zinc is oxidized to zinc ions, and hydrogen ions are reduced to hydrogen. Equation 2 can be conveniently divided into two reactions, the oxidation of zinc and the reduction of hydrogen ions:



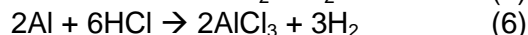
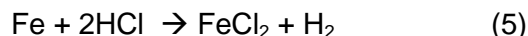
An oxidation (or anodic) reaction is indicated by a production of electrons. The consumption of electrons signifies a reduction (or cathodic) reaction. Equations (3) and (4) are partial reactions – both must occur simultaneously and at the same rate on the metal surface. If they do not occur simultaneously and at the same rate, the metal would spontaneously become electrically charged, which is impossible because of the Law of Conservation of Charge. This leads to one of the most important basic principles of corrosion: **during metallic corrosion, the rate of oxidation equals the rate of reduction**. This concept is illustrated in Figure 2.



**FIGURE 2 – Electrochemical Reactions Occurring During Corrosion of Zinc in De-aerated Hydrochloric Acid**

Here a zinc atom has been transformed into a zinc ion and two electrons. These electrons are immediately consumed during the reduction of hydrogen ions to form hydrogen gas. Figure 2 shows these two processes spatially separated for clarity. Whether or not they are actually separated, or occur at the same point on the surface, does not affect the above principle of charge conservation. In some corrosion reactions, the oxidation reaction occurs uniformly on the surface, while in other cases it is localized and occurs at specific areas.

The corrosion of zinc in hydrochloric acid is an electrochemical process. Any reaction that can be divided into two (or more) partial reactions of oxidation and reduction is termed electrochemical. Dividing corrosion or other electrochemical reactions into partial reactions makes them simpler to understand. Iron and aluminum, like zinc, are also rapidly corroded by hydrochloric acid. The reactions are:



At first sight these appear quite different. However, comparing the partial reactions of oxidation and reduction indicates that reactions (1), (5) and (6) are quite similar. All involve hydrogen ion reduction, and they differ only in their oxidation, or anodic, reactions:



Hence, the issue of hydrochloric acid corrosion is simplified since in every case the cathodic reaction is the evolution of hydrogen gas according to reaction (4). This also applies to corrosion in other acids such as sulfuric, phosphoric, hydrofluoric, and water-soluble organic acids such as formic and acetic. In each case, only the hydrogen ion is active. The other ions such as sulfate, phosphate, and acetate do not participate in the electrochemical reaction.

When viewed from the standpoint of partial reactions of oxidation and reduction, all corrosion can be classified into a few generalized reactions. The anodic reaction in every corrosion reaction is the oxidation of a metal to its ion. This can be written in the general form:

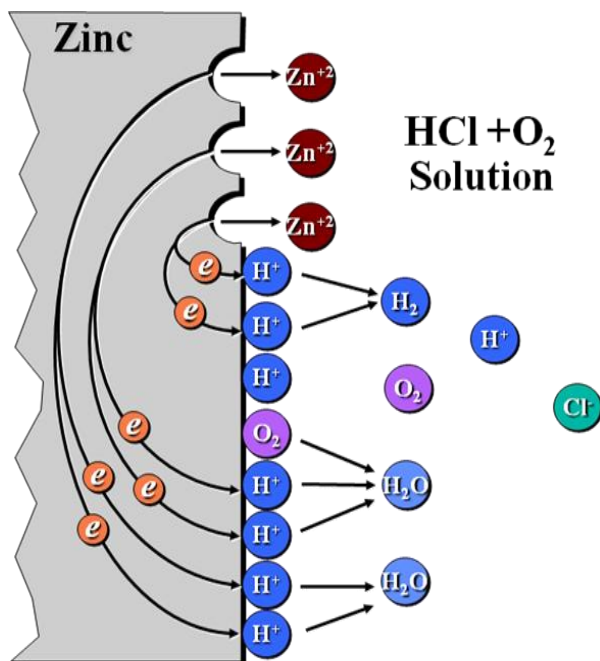


In each case, the number of electrons produced equals the valence of the ion.

There are several different cathodic reactions that are frequently encountered in metallic corrosion. The most common are:



During corrosion, more than one oxidation and one reduction reaction may occur. When an alloy is corroded, its component metals go into solution as their respective ions. More importantly, more than one reduction reaction can occur during corrosion. Consider the corrosion of zinc in aerated hydrochloric acid (Figure 3).



**FIGURE 3 – Electrochemical Reactions Occurring During Corrosion of Zinc in Aerated Hydrochloric Acid**

Two cathodic reactions are possible: the evolution of hydrogen and the reduction of oxygen. There are two electron-consuming reactions on the surface of the zinc. Since the rates of oxidation and reduction must be equal, increasing the total reduction rate increases the rate of zinc dissolution. Hence, acid solutions containing dissolved oxygen will be more corrosive than oxygen-free acid solutions.

Since the anodic and cathodic reactions occurring during corrosion are mutually dependent, it is possible to reduce corrosion by reducing the rate of either reaction. If the surface of the metal is coated with paint or another non-conducting film, the rates of both anodic and cathodic reactions will be greatly reduced, and corrosion will be retarded. However, paint films have microscopic (and sometimes macroscopic) defects which allow moisture, chloride ions, acid rain and other corrosives to pass through and contribute to corrosion of the underlying metal. Even if there are no defects in the coating, all paints are semi-permeable membranes in which corrosives can slowly migrate through and reach the surface. This phenomenon will be discussed later.



### THE ELECTROMOTIVE FORCE SERIES

If a voltmeter is connected between copper and zinc electrodes, a potential difference of approximately 1.1 volts is observed. This is the cell potential that is used in determining the free energy of the overall electrochemical reaction. To simplify the representations and calculations of cell potentials, the concept of half-cell potentials has been developed. An arbitrary half-cell reaction is used as a reference by defining its potential as zero, and all other half-cell potentials are calculated with respect to this zero reference. Although any half-cell reaction can be chosen for this standard reference point, the hydrogen-hydrogen ion reaction ( $2\text{H}^+ + 2\text{e}^- = \text{H}_2$ ) is universally accepted.

Table 1 lists the half-cell potentials for some electrochemical reactions.

**TABLE 1 – Electromotive Series of Metals**

**Standard EMF Series of Metals**



	Metal-Metal Ion Equilibrium (Unit Activity)	Electrode Potential vs. Normal Hydrogen Electrode at 25°C, Volts
 Noble or Cathodic	Au-Au <sup>+</sup>	+1.498
	Pt-Pt <sup>2+</sup>	+1.2
	Pd-Pd <sup>2+</sup>	+0.987
	Ag-Ag <sup>+</sup>	+0.799
	Hg-Hg <sub>2</sub> <sup>2+</sup>	+0.788
	Cu-Cu <sup>2+</sup>	+0.337
	H <sub>2</sub> -H <sup>+</sup>	0.000
 Active or Anodic 	Pb-Pb <sup>2+</sup>	-0.126
	Sn-Sn <sup>2+</sup>	-0.136
	Ni-Ni <sup>2+</sup>	-0.250
	Co-Co <sup>2+</sup>	-0.277
	Cd-Cd <sup>2+</sup>	-0.403
	Fe-Fe <sup>2+</sup>	-0.440
	Cr-Cr <sup>3+</sup>	-0.744
	Zn-Zn <sup>2+</sup>	-0.763
	Al-Al <sup>3+</sup>	-1.662
	Mg-Mg <sup>2+</sup>	-2.363
	Na-Na <sup>+</sup>	-2.714
	K-K <sup>+</sup>	-2.925

This table is frequently called the Electromotive Series (EMF) series. From the data presented in Table 1, it is possible to calculate the cell potential for numerous electrochemical reactions. Note that the absolute potential difference between the copper electrode and zinc electrode is approximately 1.1 volts, and that the copper electrode is positive with respect to the zinc electrode. Likewise, the potential difference between the copper and silver electrode is 0.45 volt, and copper is negative with respect to silver. Thus, this concept greatly simplifies the calculation of cell potentials.

However, in actual corrosion situations, galvanic coupling between pure metals in equilibrium with their ions rarely occurs. Most metals used industrially are alloys of two or more metals, and contain impurities. Therefore, the galvanic series in Table 2, which lists some commercial metals in seawater, is more useful.

**TABLE 2 – Galvanic Series of Commercial Metals in Seawater**

**Galvanic Series of Some Commercial Metals  
and Alloys in Seawater**

 Noble or Cathodic	Platinum
	Gold
	Graphite
	Titanium
	Silver
	18-8 Mo Stainless Steel
 Active or Anodic 	18-8 Stainless Steel
	Monel (70 Ni, 30 Cu)
	Cupronickels (60-90 Cu, 40-10 Ni)
	Bronzes (Cu-Sn)
	Copper
	Brasses (Cu-Zn)
	Inconel
	Nickel
	Tin
	Lead
	Lead-tin Solders
	Cast Iron
	Steel or Iron
	2024 Aluminum (4.5 Cu, 1.5 Mg, 0.6 Mn)
	Cadmium
	Commercially Pure Aluminum
	Zinc
	Magnesium and Magnesium Alloys

The practical value of this is in any electrochemical reaction, the most negative (or active) half-cell tends to be oxidized, and the most positive (or noble) half-cell tends to be reduced.

## FORMS OF CORROSION RELEVANT TO PAINTED METAL

There are three forms of corrosion that are relevant to painted metal. They are: galvanic, crevice, and filiform. Each of these is discussed below.

### Galvanic Corrosion

As discussed above, a potential difference usually exists between two dissimilar metals when they are immersed in a corrosive or conductive solution. If these metals are placed in contact (or otherwise electrically connected), this potential difference produces electron flow between them.

Corrosion of the less corrosion-resistant metal is usually **increased**, and attack of the more corrosion-resistant material is **decreased**, as compared with the behavior of these metals when they are not in contact. The less resistant metal becomes anodic and the more resistant metal becomes cathodic. Usually the cathode or cathodic metal corrodes very little (or not at all) in this type of couple. Because of the electric currents and dissimilar metals involved, this form of corrosion is called galvanic corrosion. The driving force for the electric current and corrosion is the potential difference developed between the two metals.

A classic example of galvanic corrosion is exhibited in galvanized steel. Galvanized steel consists of a thin zinc coating on a steel substrate. The galvanic series (Table 2) shows that zinc is more anodic (or active) than steel. Therefore, when these two metals are connected in the presence of an electrolyte (e.g., moisture), the zinc will corrode preferentially, and thus protect the steel from corrosion (see Figure 4).

## Cathodic Protection

- Make Part Cathode of Galvanic Cell  
– Galvanized Steel

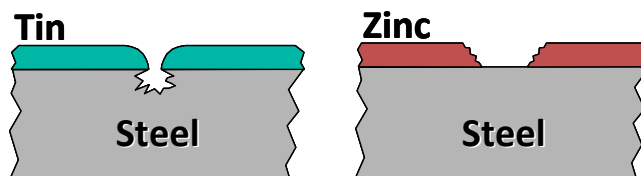


FIGURE 4 – Galvanic Corrosion

The zinc will corrode faster (and the steel slower) than if the two metals were exposed to the same environment, but not coupled! Thus, galvanized steel is an example of how galvanic corrosion can be advantageous.

Conversely, tin-plated steel represents the opposite effect (Figure 4). Table 2 shows that tin is noble (or cathodic) to steel. Therefore, when these two metals are connected in the presence of an electrolyte

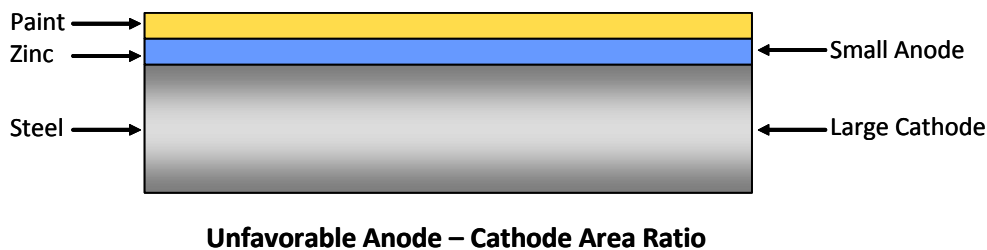
(e.g., soup in a tin can), the steel will corrode preferentially to the tin coating, if there is a pin hole or defect in the tin coating. This preferential corrosion of the steel can result in accelerated perforation of the can. This is a case where galvanic corrosion is not favorable.

The severity of galvanic corrosion depends largely on the type and amount of moisture present. For example, corrosion is greater near a sea shore than in a drier rural atmosphere. Condensate near a sea shore contains salt, and therefore is more conductive and corrosive. Atmospheric exposure tests in different parts of the country have shown zinc to be anodic to steel in all cases, aluminum varied depending on environmental conditions, and tin and nickel were always cathodic. Galvanic corrosion does not occur when the metals are completely dry since there is no electrolyte to carry the current between the two electrode areas.

**Distance Effect.** Accelerated corrosion due to galvanic effects is usually greatest near the bi-metal junction, with attack decreasing with increasing distance from that point. The distance affected depends on the conductivity of the solution. This is why the corrosion of galvanized steel is greatest at the cut edge (i.e., where zinc coating and steel substrate both are exposed to the electrolyte).

**Area Effect.** Another important factor in galvanic corrosion is the area effect, or the ratio of the cathodic to anodic areas. An unfavorable area ratio consists of a *large* cathode and a *small* anode. For a given current flow in the cell, the current density is greater for a smaller electrode than for a larger one. The greater the current density at an anodic area, the greater the corrosion rate. Corrosion of the anodic area may be 100 to 1000 times greater than if the anodic and cathodic areas were equal in size. The area effect of galvanic corrosion is a contributing factor to the so-called “cut edge” corrosion of painted metal (see Figure 5).

### Prepainted Galvanized Steel at Cut Edge



**FIGURE 5 – Area Effect of Galvanic Corrosion**

When galvanized steel is painted, an unfavorable anode-cathode area ratio exists at the cut edge (i.e., small anode from the zinc surface; large cathode from the steel substrate). This unfavorable ratio can contribute to accelerated corrosion of the zinc, causing blistering and delamination of the paint film.

### Crevice Corrosion

Intensive localized corrosion frequently occurs within crevices and other shielded areas on metal surfaces exposed to corrosives. This type of attack is usually associated with small volumes of stagnant solution caused by holes, gasket surfaces, lap joints, surface deposits, and crevices under bolt heads. As a result, this form of corrosion is called *crevice corrosion*. Examples of deposits that may produce corrosion are sand, dirt, corrosion products, and other solids. The deposit acts as a shield and creates a stagnant condition.



To function as a corrosion site, a crevice must be wide enough to permit liquid entry, but sufficiently narrow to maintain a stagnant zone. For this reason, crevice corrosion usually occurs at openings of 50 – 100 µm or less in width. It rarely occurs within wide (e.g., 3 mm) grooves or slots. Fibrous gaskets, which have a wick action, form a completely stagnant solution in contact with a flange face. This condition forms an almost ideal corrosion site.

Crevice corrosion conditions can commonly occur with painted metal. Examples include:

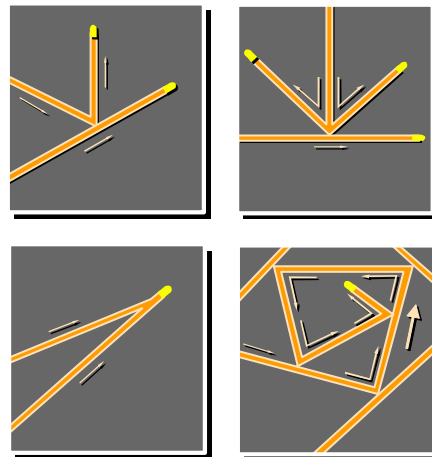
- At fasteners, particularly if they are over-driven to indent and create a liquid reservoir. A clear manifestation of this is the paint blistering seen around fasteners on pre-engineered metal buildings.
- At lap joints
- Under surface deposits (e.g., dirt, accumulation of glass clippings, etc.)

### Filiform Corrosion

Filiform corrosion (filamentary corrosion occurring on metal surfaces) is a special type of crevice corrosion. In most instances, it occurs under paint films. However, filiform corrosion has also been observed on steel, magnesium, and aluminum surfaces covered by tin, silver, or gold. Filiform corrosion is an unusual type of attack, since it does not weaken or destroy metallic components, but only affects surface appearance. The attack appears as a network of corrosion product trails. The filaments consist of an active head and a corrosion product tail, as illustrated in Figure 6.

## Filiform Corrosion

- Corrosion “Filaments”  
– wormlike
- Occurs under paint
- Aesthetic problem



**FIGURE 6 – Filiform Corrosion**

The filaments are 3 mm or less wide, and corrosion occurs only in the filament head.

Interaction between corrosion filaments is most interesting. Corrosion filaments are initiated at edges and tend to move in straight lines. Filaments do not cross tails of other filaments. The most important environmental variable in filiform corrosion is the relative humidity of the atmosphere. Filiform corrosion occurs primarily between 65% and 90% relative humidity. If relative humidity is lower than 65%, the metal is unaffected. At more than 90% humidity, corrosion primarily appears as blistering. Studies have shown that the type of protective coating on a metal surface is relatively unimportant, since filiform corrosion has been observed under paint and metallic coatings. However, coatings with lower water permeability suppress filiform corrosion.

Filaments tend to follow grinding marks and polishing direction (i.e., high energy surface sites which are anodic and prone to be active corrosion sites).

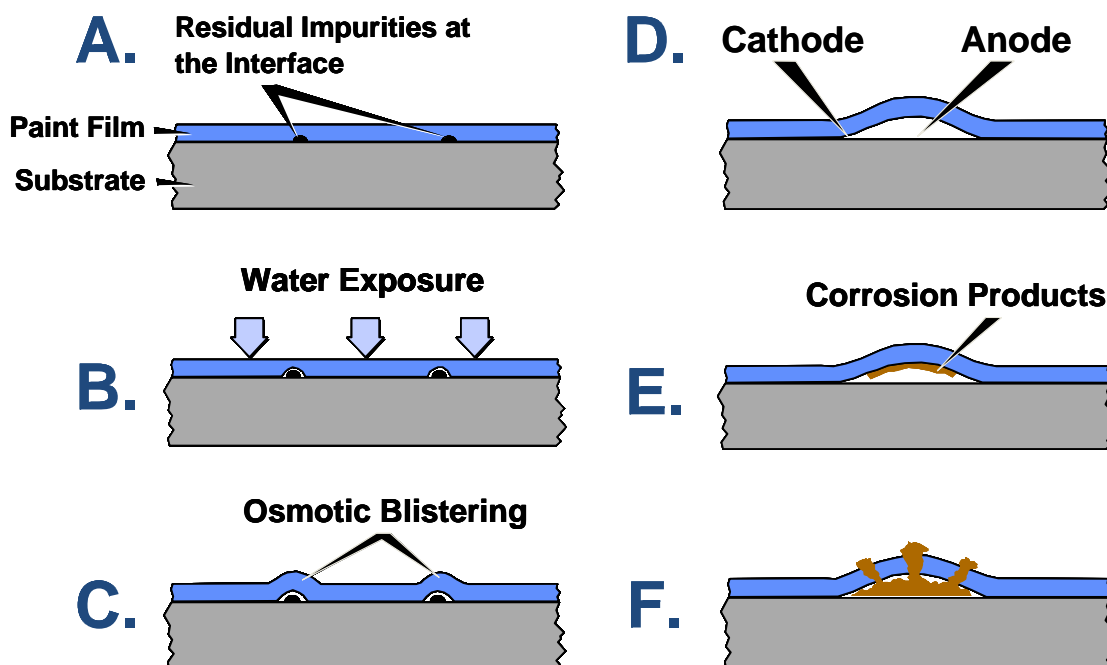
The most common instance of filiform corrosion of painted metal is on aluminum or steel used or stored in humid environments (e.g., washing machines; building components such as eaves or gutters and downspouts). There is no completely satisfactory way to prevent filiform corrosion. Two approaches to minimize it are to store and use painted metal in low humidity environments, and to use paint coatings of very low moisture permeability.

## CORROSION MECHANISMS OF PAINTED METAL

The following will discuss three of the most common corrosion mechanisms of painted metal: (a) blistering; (b) cathodic delamination; and (c) anodic delamination.

### Paint Blistering

Paint blistering due to corrosion starts with a defect – usually on the metal surface (see Figure 7A).



**FIGURE 7 – Paint Blistering Mechanism**

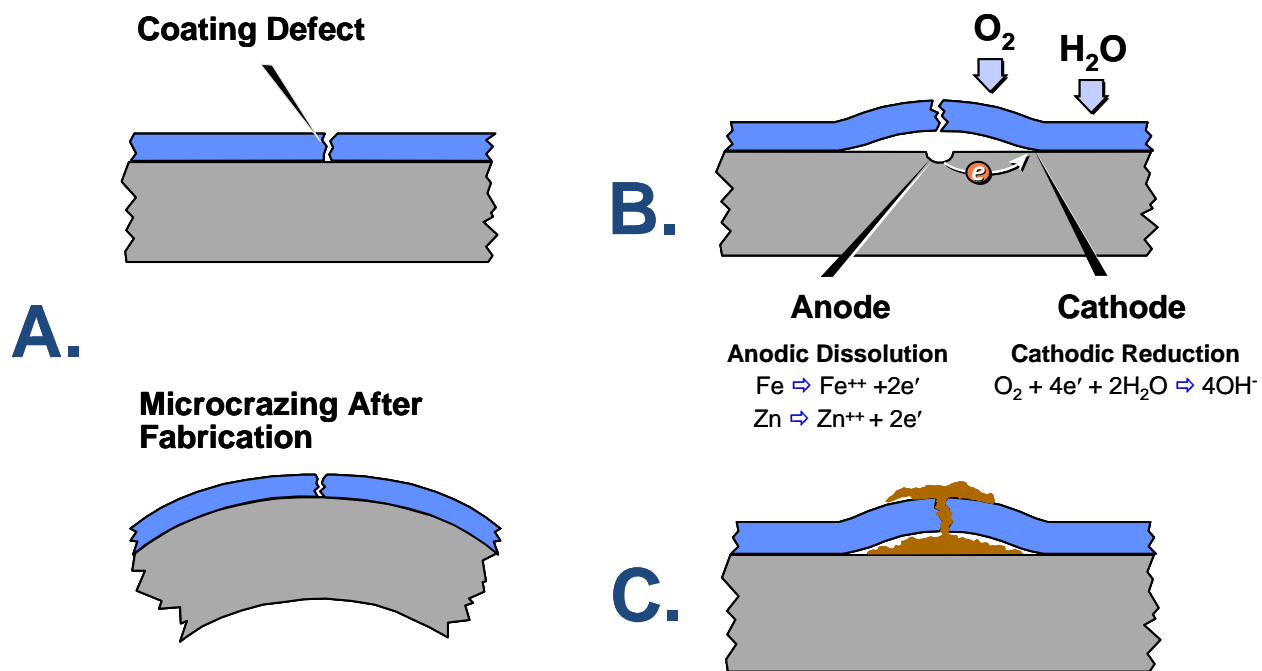
The defect can be due to one or more of the several sources: (a) residual impurities on the metal surface – such as residual hard water salts from process water, residual soils from inadequate cleaning of the metal surface, unreacted pretreatment chemicals, etc.; (b) residual solvent from the paint itself; (c) impurities on the metal substrate itself – such as oxides, inclusions, etc.; and (d) high energy sites on the metal surface such as scratches, polishing/grinding marks, mill roll marks, etc. All these defects are possible sites for paint blistering because all paint coatings are semi-permeable membranes. Thus there is a driving force for water (assuming there is moisture in the atmosphere) to equalize pressure at both sides of the paint film (i.e., the air-paint interface, and the paint-substrate interface). Water is going to be drawn to the paint-substrate interfacial defects by osmosis (Figure 7B). Eventually, the moisture build up is so great, the force breaks the interfacial bonds and lifts the paint from the substrate,

resulting in blistering (Figure 7C). The literature has reported that the pressure that forms at the interface of these so-called osmotic blisters could be anywhere from 200-500 psi.

Typically, but not always, the center of the defect becomes the anode of a corrosion cell. The area at the advancing interface of the blister becomes the cathode (Figure 7D). Formation of corrosion products occurs (Figure 7E), and eventually the corrosion products become voluminous enough to break through the paint film and give us an unsightly appearance (Figure 7F).

### Cathodic Delamination

Another common paint failure mechanism is cathodic delamination. As the name would imply, it's driven by the cathodic reactions of an electrochemical corrosion cell. This might start with the coating defect in the paint film, or perhaps a micro-crack in the paint film after a fabrication step (Figure 8A).



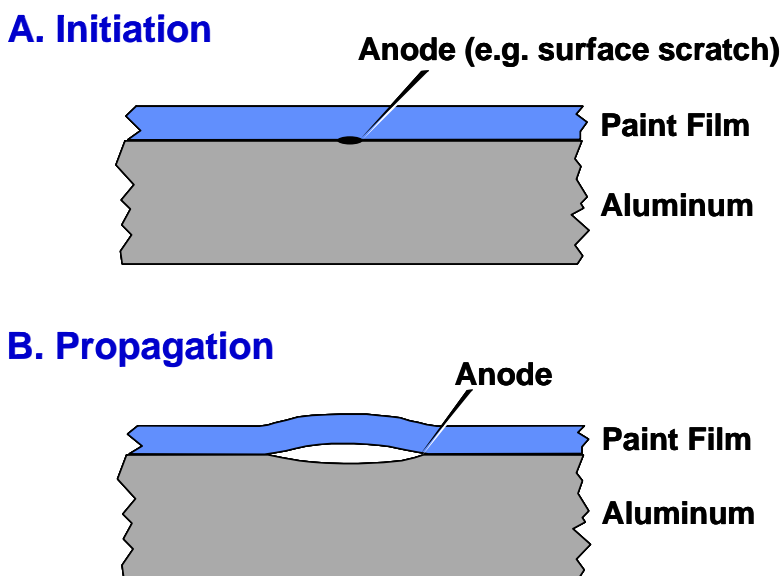
**FIGURE 8 – Cathodic Delamination**

Typically, that defect area becomes the anode of an electrochemical corrosion cell. Figure 8B gives examples of the types of reactions that can occur at the anode (i.e., dissolution of the metal into its ions, and the liberation of electrons). The electrons would transmit through the metal to the advancing interface, and take part in a cathodic reduction reaction. The particular cathodic reaction shown in Figure 8B is the reduction of oxygen in a neutral or basic solution. It raises the pH to about 11-12. This high a pH will solubilize the interfacial bonds and cause additional paint lifting. Eventually, corrosion products will start to protrude through the paint surface (Figure 8C). Cathodic delamination is very common in cold-rolled steel, and also in zinc-coated surfaces such as galvanized, electro-galvanized, and Galvalume steel.

### Anodic Delamination

Conversely, a very common failure mechanism of painted aluminum is anodic delamination. Again, it all starts with a defect – a microscopic defect which becomes the anode of an electrochemical

corrosion cell (Figure 9). The propagation of paint lifting with aluminum is typically caused by anodic delamination



**FIGURE 9 – Anodic Delamination**

(i.e., the advancing interface of the anode). The oxide layer on a material such as aluminum is consumed by the anodic reaction, destroying the adhesion between the paint and substrate.

It is obvious in all these failure mechanisms that the permeability through the paint film, and interfacial bonding are two of the most important characteristics to control the corrosion of painted metal.

### **KEY POINTS TO CONTROL CORROSION OF PAINTED METALS**

As noted earlier, reducing either the cathodic or anodic reaction will reduce the overall corrosion rate of the system. From a practical standpoint, this can be accomplished in several ways, as noted below.

- Lower the permeability of the paint film. Lowering the permeability of oxygen, moisture, and other corrodents through the paint film will mitigate filiform corrosion, paint blistering, and cathodic and anodic dissolution.
- Minimize defects on the metal substrate surface. Defects on the metal surface such as grinding or polishing marks, mill roll marks, nonmetallic inclusions, oxides, grain boundaries, nicks, and scratches are high energy sites which can drive the anodic reaction and accelerate corrosion under the paint film.
- Minimize residual salts and chemical impurities on the metal surface. The cleaning and pretreatment steps prior to painting can leave hard water salts from rinsing or process water in general, and/or chemical contaminants from unreacted pretreatment chemicals that are not adequately removed by rinsing. Also, inadequate cleaning can leave residual soils on the metal substrate surface. These chemical impurities attract moisture permeating through the paint and can lead to osmotic blistering of the paint (see Figure 7).

- Adequately bake/cure the coating. Residual solvents or water remaining in the paint from incomplete baking/curing are defect sites that are prone to blistering.
- Avoid crevices, particularly those less than 100  $\mu\text{m}$ . Small crevices are prone to retention of moisture and other corrosives which accelerate corrosion. Also, keeping the painted surface clean of deposits such as mud and dirt will mitigate the propensity of crevice corrosion.
- Avoid dissimilar metals in contact with each other. Dissimilar metals which are electrically coupled by simple contact drive galvanic corrosion, particularly in the presence of an electrolyte such as salt water.
- Avoid unfavorable anode to cathode ratios. A small anode to large cathode ratio greatly accelerates the corrosion rate of the anode. Examples of an unfavorable ratio include holidays in the paint film, and cut edges of painted steel that is coated with a metal coating (Figure 5).
- Avoid micro-cracks in the paint film. Micro-cracks lead primarily to cathodic delamination (Figure 8), but can contribute to other corrosion mechanisms also. Micro-cracks occur because the paint film lacks flexibility or toughness, causing micro-cracks to develop: (a) during forming of the painted metal after painting; (b) from residual stresses in the paint; and/or (c) from differences in thermal expansion between the paint and the primer or metal substrate.

## **SPECIFIC EXAMPLES OF HOW NANOCOMPOSITE COATINGS IMPROVE THE CORROSION RESISTANCE OF PAINTED METALS**

### **Experimental Procedures**

Cathodic Disbondment Test: Steel test panels (5 mm x 10 mm) were grit blasted to a SSPC (Steel Structures Painting Council) SP-10 (near white surface with at least 95% of the surface being perfectly clean) or SP-6 (at least 65% of the surface free of mill scale, oxides, and general soil). A proprietary non-chromium nanocomposite pretreatment designed for use on steel was applied to the panels that were blasted to SP-6. A Navy high solids epoxy primer (MIL-PRF -23236C) was then applied to the steel at  $\sim 100\ \mu\text{m}$  thickness, and air dried for one week prior to testing.

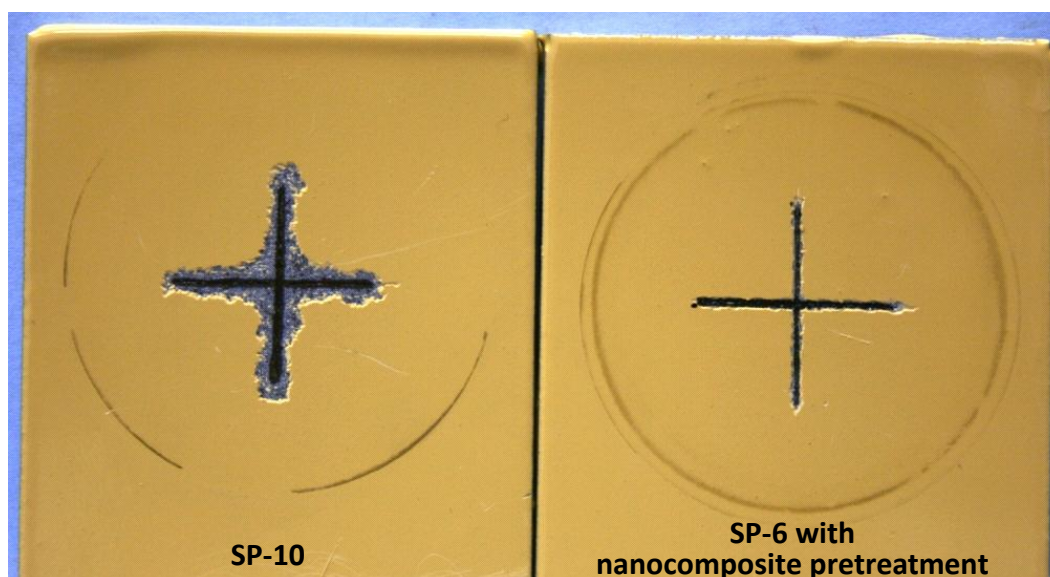
The cathodic disbondment test involved scribing the sample through the epoxy primer down to the bare metal. The scribe marks were made at right angles to form a 2 x 2 cm cross using a razor blade. An electrochemical cell, filled with a 3.5 wt% NaCl aqueous solution, was then placed over the cross and a voltage of -0.59 V (cathodic polarization) versus SCE reference electrode was applied for 24 hours. After the cathodic treatment, the coating along the scribe was removed with a razor blade to reveal the extent to which cathodic polarization produced disbondment.

Anodic Disbondment Test: Aluminum test panels (5 mm x 10 mm) were grit blasted to a SP-10 finish. A proprietary non-chromium nanocomposite pretreatment designed for use on aluminum was applied to one set of panels. The panels were then painted with a yellow epoxy primer (MIL-PRF-23236C) at  $\sim 100\ \mu\text{m}$  and a grey silicone alkyd topcoat (MIL-PRF-24635C) at  $\sim 50\ \mu\text{m}$ . After painting, the panels were air dried for one week prior to testing. A cross scribe was then made in the paint through to the aluminum substrate. The panels were then subjected to salt spray testing (ASTM B-117) for 28 days.

### **Results**

Nanocomposite Pretreatment on Steel to Inhibit Cathodic Delamination: Figure 10 gives the results of the cathodic disbondment test. This is a severe test required by the U.S. Navy to assess the ability

of paint coatings to resist corrosion failure by cathodic delamination when subjected to severe marine environments typically encountered by Navy ships and structures. Figure 10 clearly shows the advantage of using the proprietary Nanomyte® non-chromium nanocomposite pretreatment developed by NEI Corporation to mitigate corrosion by inhibiting the cathodic reactions. That is, the level of paint removal at the scribe area is much lower for the sample with the nanocomposite pretreatment compared to the sample without the pretreatment. It is also significant to note that the sample with the nanocomposite pretreatment was applied to a steel surface with a much lower amount of grit blasting (SP-6, which requires that only 65% of the surface be free of mill scale, oxides, and general soil) compared to the control sample which had no pretreatment, but which was blasted to a much higher level of surface cleanliness (SP-10, which requires a near white surface with at least 95% of the surface being perfectly clean). This pretreatment has the potential for the Navy to improve the corrosion resistance of painted surfaces, while at the same time reducing the amount of grit blasting. Grit blasting is a costly and environmentally unfavorable process because it generates huge quantities of hazardous powdery waste.



**Scribed sample in 3.5% NaCl under -0.59V cathodic polarization for 24 hours**

**FIGURE 10 – Cathodic Disbondment Test**

Nanocomposite Pretreatment on Aluminum to Inhibit Anodic Delamination. Figure 11 shows 28 day salt spray results of grit blasted aluminum panels that were coated with a yellow epoxy-polyamide primer (MIL-PRF-23236C) and a grey silicone alkyd topcoat (MIL-PRF-24635C) – both used by the U.S. Navy. The panel on the right has a proprietary non-chromium nanocomposite pretreatment applied to the aluminum surface prior to painting. The panel on the left does not have the nanocomposite pretreatment. Figure 11 shows much less paint failure for the sample with nanocomposite pretreatment, and demonstrates the ability of the proprietary nanocomposite pretreatment to mitigate anodic delamination on aluminum. The nanocomposite pretreatment used in this test was designed for use on aluminum, whereas the nanocomposite pretreatment used on steel was designed for use on steel; obviously, they are different formulations.





**Paint Applied Over Grit Blasted Aluminum**



**Paint Applied Over Grit Blasted Aluminum  
with Nanocomposite Pretreatment**

**FIGURE 11 - Coated Aluminum Panels After 28 Days Salt Spray Test. A Yellow Primer and Grey Topcoat Were Used.**

## **CONCLUSIONS**

Corrosion is a ubiquitous and on-going problem. It causes tens of millions of dollars of damage annually, and compromises the safety, environmental, and aesthetic characteristics of the affected structures.

Metals ordinarily exist naturally as oxides (i.e., ore) because oxides represent their lowest energy state. However, after the oxides are removed from the ground, they are processed into useful industrial metals by various techniques such as refining, casting, and forming. These metals are now in an “activated” state and are thermodynamically unstable and predisposed to return to their natural oxide state. Inorganic (metal) and organic (paint) coatings are frequently applied to mitigate corrosion, which is the transformation of metals back to their natural oxide state.

Corrosion in the presence of moisture is an electrochemical process which can be described by two separate reactions – an oxidation (anodic) reaction and reduction (cathodic) reaction. The physical Laws of Conservation of Charge dictate that the rate of oxidation must equal the rate of reduction. Therefore, controlling either the rate of oxidation or the rate of reduction will lower the overall corrosion rate of the system in question. Newly developed, non-chromium nanocomposite coatings were shown

to effectively reduce either the anodic or cathodic reactions to lower the overall corrosion rate of the material.

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