102

Corrosion and Its Control by Coatings

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102.1 Introduction

102.1.1 Energy Transfer

The metallic state is in most metals an unstable condition resulting from the smelting operation, in which energy is imported by the ore as the metal is derived. After extraction, most metals undergo a slow deterioration process during which they shed this energy and return to a more stable condition in which they are combined with some element of their environment, such as an oxide, a sulfide, or some other corrosion product. This energy conversion process is known as corrosion.

102.1.2 The Electrochemical Nature of Corrosion

Corrosion is most usually driven by some electrochemical inhomogeneity in the metal or its environment. In this process, different areas of the metal, having different levels of free energy and therefore different corrosion potentials, become the electrodes of an electrochemical cell in contact with a common electrolyte.[1–5] The electrochemical couples are set up with areas of more active electrochemical potential acting as anodes of the cell, while more passive areas act as cathodes (Figure 102.1). Corrosion takes place at the anodes as metal dissolves into the electrolyte as ions, so releasing electrons, which pass through the metal to the adjacent cathode areas where they react with the environment. This flow of electricity, the electron passage from anode to cathode, and the accompanying charge transfer back through the electrolyte from cathode to anode, make up the corrosion current. The rate of the current flow, i.e., the magnitude of the corrosion current (I) that develops, is a measure of the amount of degradation and is related to the potential difference (V) between the anodic and cathodic sites by Ohm's law:

$$I = \frac{V}{R} \tag{102.1}$$

where R is the total resistance of the cell.

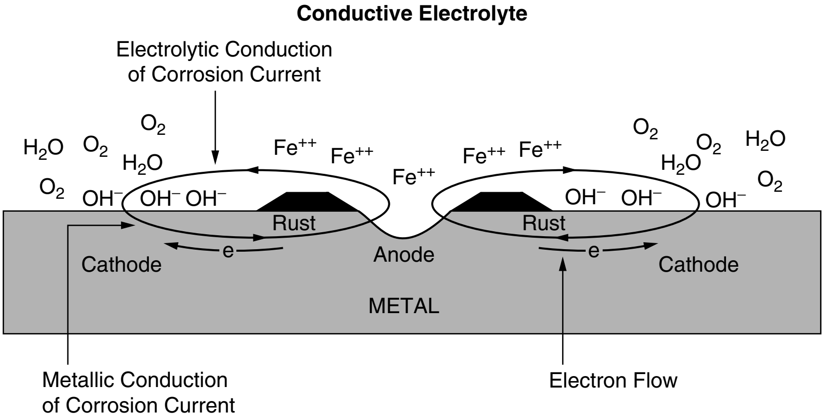

FIGURE 102.1 Electrochemical corrosion cell.

In the normal corrosion cell, R is in fact made up of several individual resistances: the resistances of the two electrodes (R_a and R_c), the resistance of the internal electrical contiguity between them, R_w, and the electrolytic resistance of the common electrolyte across their external faces, R_e.

Ohm's law may thus be rewritten

$$I = \frac{V}{R_a + R_c + R_w + R_e} \tag{102.2}$$

As the anode, the cathode, and their contiguity are all metallic, these resistances are negligible compared to the resistance of the electrolyte, which is ionic, and which may be exceedingly high in electrolytes of low ionic content (e.g., deionized water). The resistances of salt solutions, however, are much lower. It is for this reason that corrosion proceeds much faster in seawater, and only very slowly in freshwater.

Because of these things, the relationship shown in Equation (102.2) becomes practically equivalent to

$$I = \frac{V}{R_e} \tag{102.3}$$

Minimization of the conductivity of the electrolyte is, therefore, an important maxim in corrosion control.

Equally important, of course, is the minimization of V. All metals have different electrode potentials (see Table 102.1), and large potential differences are set up where the electrochemical cell is composed of different metals. The electrical contiguity of a more noble metal and an active one in contact with the same electrolyte can produce severe galvanic corrosion in the active metal. On the other hand, the deliberate electrical fixation of a more active metal (such as zinc) to one of more passive potential (steel) is a powerful stratagem that is widely employed to eliminate corrosion in the passive material in the presence of a common electrolyte. Zinc, magnesium, and rarely aluminum anodes (generally ingots or in the case of zinc often films) are widely used to protect steel in this manner.

Table 102.1 lists many common metals in terms of their electrochemical potential. Those having extremely positive electropotentials (gold, platinum, etc.) are very stable and do not corrode. They are found in nature in the metallic state.

102.1.3 Electrode Reactions

The chemical reaction at the anode (the dissolution of the metal) may be written

TABLE 102.1 Electrode Potentials

Electrode Reaction			Potential (volts)
	Active		
Na	⇔	$Na^+ + e$	–2.71
Mg	⇔	$Mg^{+2} + 2e$	–2.38
Al	⇔	$Al^{+3} + 3e$	–1.66
Zn	⇔	$Zn^{+2} + 2e$	–0.76
Fe	⇔	$Fe^{+2} + 2e$	–0.44
Pb	⇔	$Pb^{+2} + 2e$	–0.13
H	⇔	$H^+ + e$	0.00
Cu	⇔	$Cu^{+2} + 2e$	0.34
Ag	⇔	$Ag^+ + e$	0.80
Pt	⇔	$Pt^{+2} + e$	1.2
Au	⇔	$Au^{+3} + 3e$	1.4
	Noble (Passive)		

$$M = M^{n+} + ne \tag{102.4}$$

where n is the valency of the metal.

In the case of iron, this equation becomes

$$Fe \rightarrow Fe^{2+} + 2e \tag{102.5}$$

The exact nature of the reaction at the surface of the cathode (in which electrons released in anodic dissolution are, in turn, consumed) depends upon the nature of the environment. Under neutral and alkaline conditions, the reaction involves oxygen and proceeds

$$2H_2O + O_2 + 4e = 4OH^- \tag{102.6}$$

Under acidic conditions, if oxygen is present, the reaction may proceed

$$O_2 + 4H^+ + 4e = 2H_2O \tag{102.7}$$

Where oxygen is not available, hydrogen gas may form under acidic conditions:

$$2H^+ + 2e = H_2 \tag{102.8}$$

Migration of the oxidative product (M^{n+}) from the anode and the reduction product (OH^-) from the cathode occurs until they combine to form the oxide, which precipitates. In the case of steel this may be $Fe(OH)_2$, ferrous hydroxide, or, depending upon the nature of the environment, one of several precursor products, such as ferrous hydroxy chloride in salt water. Ferrous products are readily soluble, and this favors migration, so that oxide formations are not intimately associated with the anode but are loosely adherent and porous. Given sufficient oxygen, a second oxidation reaction will occur in steel corrosion, which converts the divalent ion to the trivalent ferric state,

$$Fe^{2+} \rightarrow Fe^{3+} + e \tag{102.9}$$

The solubility of the trivalent corrosion product is much less than that of the ferrous product. Under normal circumstances, however, where the secondary oxidative process occurs gradually after the ferrous ions have migrated away from the anode, the corrosion product is no more tightly adherent than is the ferrous product from which it is formed, and films of rust, hydrated ferric oxide ($Fe_2O_3 \times H_2O$), are usually loose and crumbly.

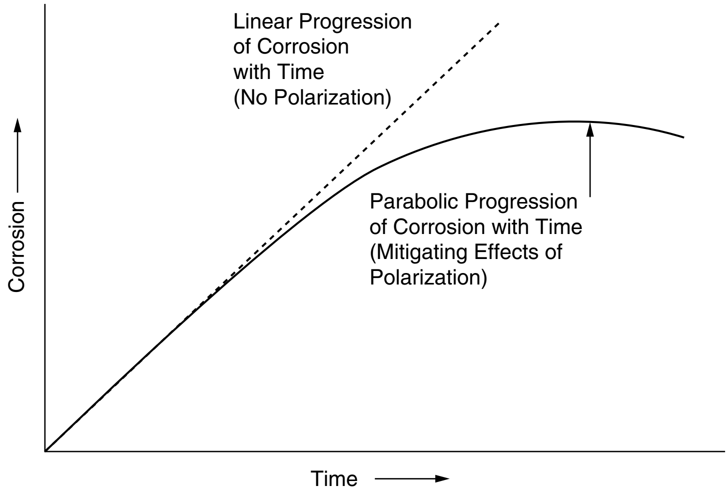

FIGURE 102.2 Polarization and its effect on corrosion rate.

102.1.4 Polarization

The accumulation of ions at the anode tends to insulate the metal from the electrolyte and reduce the amount of ions going into solution. In effect, the anode deposit or film increases the resistance of the electrochemical cell, and the cell is said to be anodically "polarized." Similarly at the cathode, cathodic films are possible. In oxygen-deprived systems, for example, hydrogen gas may accumulate at the cathode, preventing further access of hydrogen ions and the consumption of electrons. The cathode reaction is therefore stifled, and the metal is said to be cathodically polarized. (Where oxygen levels are high enough, the cathode reaction occurs irrespective of the amount of H^+ ions, and in this case, the oxygen is said to have depolarized the cathode, allowing increased corrosion.)

The presence of these electrode films has a great effect on the rate of corrosion current transfer (i.e., the rate at which corrosion occurs). This can be illustrated in the resultant modification of the Ohm's law Equation (102.3). Thus,

$$I = \frac{V}{R_{\mathrm{af}} + R_{\mathrm{cf}} + R_{\mathrm{e}}} \tag{102.10}$$

where R_{af} and R_{cf} represent the resistances of the anode and cathode films, respectively. These resistances may be very high, and as such polarizing films build up, the rate of corrosion is greatly diminished (see Figure 102.2).

102.1.5 Electrode Film Breakdown and Depolarization

The permanence of such films has great significance to the control of corrosion of a specific metal. On aluminum, for example, under near neutral conditions, the naturally formed anode oxide film is very dense and insoluble (if thin) and quite resistant to mechanical removal. R_{af} becomes very high, and I becomes negligible. Aluminum, therefore, is quite resistant to corrosion under neutral conditions.

Where the environment is sufficiently acidic or alkaline, however, the oxide film on aluminum is chemically dissolved. Thus, the metal is stripped of polarizing film (depolarized) and corrodes rapidly, i.e., the cell reaction resumes its linear relationship between corrosion and time.

On other metals such as steel, the oxide film is normally less adherent and easily dislodged mechanically. Such physical removal of the oxide film has the same result as chemical removal, the corrosion rate becoming more linear until additional corrosion product can repair the site of removal, and repolarization occurs. Mechanical agitation can also depolarize the cathode. If, under acidic conditions, the cathode, polarized with hydrogen gas, is rapidly agitated in the electrolyte, the physical shearing stresses will dislodge the bubbles of hydrogen, and the cathode will again be accessible to hydrogen ions from the electrolyte. Electrons will again be consumed, and corrosion will, as a consequence, increase.

If the secondary oxidative process on iron [see Equation (102.9)] can be engineered to occur rapidly and close enough to the anode, a more adherent, denser, and more permanent barrier film of hydrated ferric oxide will be formed across the anode. This effectively prevents further dissolution of the iron into the electrolyte and greatly increases the resistance of the anode film. Under these conditions, the metal behaves as if it were more noble than it actually is. This phenomenon is known as passivation, and the thin anode films involved are known as passive films.[6,7]

102.1.6 Passivation and Depassivation

Certain materials such as chromates, phosphates, and molybdates are known to induce passivity artificially.[6–10] These materials, known as corrosion inhibitors, if present as soluble ions within the electrolyte, will adsorb onto the metal surface, reinforce the natural oxide layer, and facilitate the passive state. Other materials, most commonly soluble chlorides and sulfates, effectively compete with inhibitive ions for adsorption onto the metal surface and tend to prevent passivity thereby.[10] These salts are known as depassivating agents. The ratio of passivating ions to depassivating ions in any interfacial electrolytic environment will dictate the effectiveness of induced corrosion control.

Other factors will also affect the rate of corrosion. The passive state is more readily achieved under alkaline conditions, and, at high enough pH, oxygen alone will induce passivity without benefit of other inhibitors. Corrosion will increase on the other hand as the temperature of the system increases.

102.1.7 Area Effects

If the rate of corrosion is largely dependent upon the rate at which electrons from the anode are consumed by the cathode reaction, then the intensity of attack is dependent upon the ratio of the areas of cathode and anode sites (Figure 102.3).[1,4] Where an anode is large compared to a given cathode, the effects of the corrosion current generated will be spread over the large anode area, so that corrosion is more general

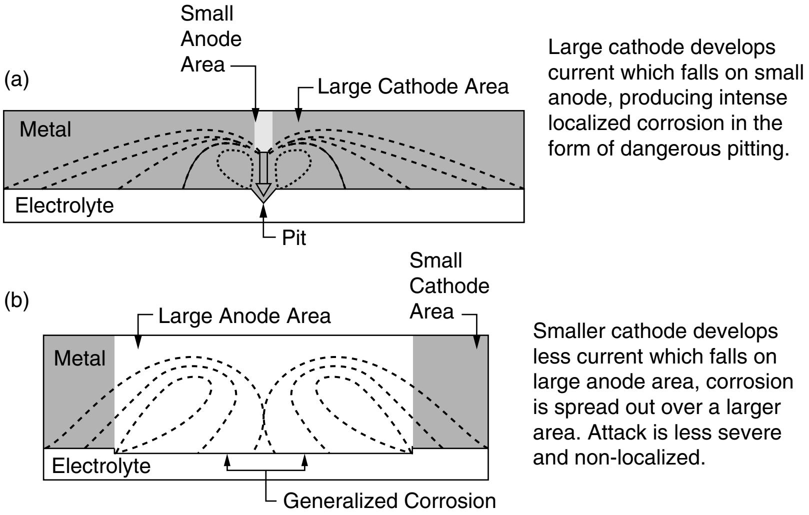

FIGURE 102.3 Area effects.

TABLE 102.2 Basic Techniques Employed in Corrosion Control by Coatings

Barrier coatings	Resistance inhibition; oxygen deprivation
Inhibitive pigments	Modification of interfacial environment (establishment of passive films)
Zinc-rich coatings	Prevention of current discharge from metal to environment by affixation of anode film

and attenuated. This type of corrosion, while undesirable, is not particularly dangerous. When the anode is small compared to the cathode, however, the current fall will be concentrated on a small area, and here corrosion will be intense. If the anode is small enough, this may lead to pitting attack, which is very dangerous and can perforate metal in a short time frame, especially where there is appreciable difference between anode and cathode potentials. Control of the area ratio is a most important consideration in corrosion engineering, and coating films may be effectively employed to modify this ration. Diminishment of the cathode area must always receive first priority in any design. Holiday detection, to eliminate anodic pinholes at which pitting may occur, is a critical quality assurance process in the application of barrier coatings.

102.2 Coatings

102.2.1 Corrosion Control by Coatings

Coatings play an important role in corrosion control, used either alone or as part of an overall strategy of corrosion control.[11] While theoretically, coatings may be employed in a variety of ways to modify, hinder, or thwart the corrosion reaction, three or four devices find practical application (see Table 102.2).

These devices are utilized in the three types of coatings employed in corrosion control.[11,12] There are barrier coatings, functioning via resistance inhibition[12,13,15,16] and/or oxygen deprivation,[14,15] inhibitive coatings, functioning by modifying the interfacial chemical environment against the metal surface,[7,8,9,11] and zinc-rich coatings, which prevent current discharge from the steel to the environment by employing a more anodically active metal (almost exclusively zinc) as a pigment at loadings high enough to ensure electrical contiguity with the substrate and low electrical resistance across the film.[17]

102.2.2 Barrier Coatings

It is a practical impossibility to prevent enough moisture transmission through even the densest films to control the cathode reaction by moisture deprivation.[12,18,19] It is, however, possible by the use of impermeable barrier coatings to suppress both oxygen transmission and the transmission of ionic solutions to a sufficient extent that corrosion may be precluded.[12,14,15,16] The prevention of oxygen access to the metal deprives the cathode reaction of critical fuel, and the film's resistance to ionic transfer renders any moisture that does access the substrate so high in resistivity that current transfer between the anodic and cathodic areas is frustrated (Figure 102.4).

Designing devices to utilize these precepts involves the use of molecularly dense films (highly uniform cross-linked thermosets and relatively crystalline thermoplastics).[12] These coatings are formulated with nonhydrophilic components and lamella pigments to give coating systems of high electrical resistance that maintain adhesion even under wet conditions.[19,20] They are typified by fluoropolymers, highly cross-linked epoxies, and coal tar modified systems, pigmented with pigments such as aluminum flake.

Barrier coatings can be used alone or in combination with impressed current driven cathodic protection systems, where they act to minimize exposed cathode areas and thereby reduce the cost of required electricity that maintains the direction of current flow.[11] Barrier coatings can also be used to minimize cathode–anode area ratios in mixed metal systems where insulation is impractical, thereby eliminating pitting at exposed anodes.

Barrier coatings are widely used for extreme service such as the lining of water, fuel, food, and chemical storage tanks, for marine coatings, etc.

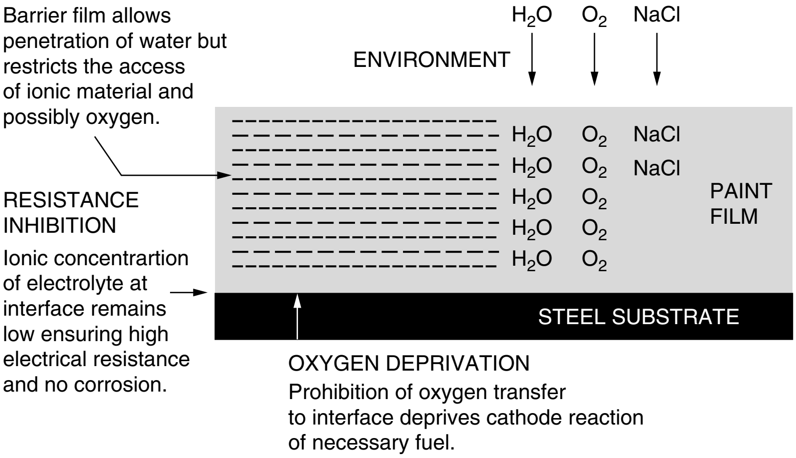

FIGURE 102.4 Corrosion control by barrier coatings.

102.2.3 Inhibitive Coatings

Inhibitive metal primers reduce corrosion by chemically modifying the interfacial condition against the metal.[7–9] This is done by including pigments in the primer film that release oxidizing ions and other passivating moieties into the aqueous phase against the interface.[11] Reviews of pigments used in this manner may be noted in Refs. 21 and 22. In turn, this reduces the levels of electrolytic oxygen necessary to establish passive films on the metal[5] beneath the coating (Figure 102.5). In order to minimize blistering and provide sufficient inhibitive ions to achieve long-term passivity without rapidly exhausting the available ionic reservoir (provided by the pigment), selection of both binder and inhibitive pigment is critical. Control of the PVC/CPVC is also important in order to maintain permeability so that there is sufficient moisture to access and dissolve enough inhibitive ions from the pigment in the film, but not so much that the film becomes too porous. Highly porous films will allow the transmission of depassivating ion species (chlorides and sulfates) into the film and through to the metal, there to compete with inhibitive ions for adsorption and so prevent passivation.[9,11]

Inhibitive coatings are generally oleoresinous systems, oils, alkyds, epoxy esters, phenolic varnishes, etc., although epoxies and many latex primers also function by this mechanism. Inhibitive coatings are

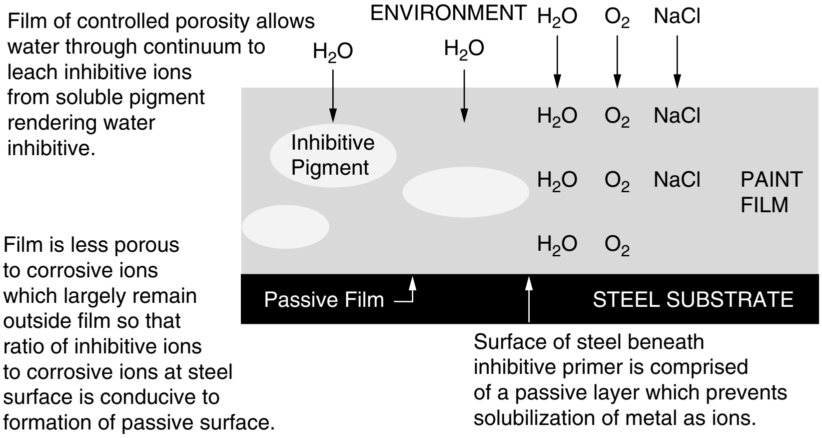

FIGURE 102.5 Corrosion protection by inhibitive primer.

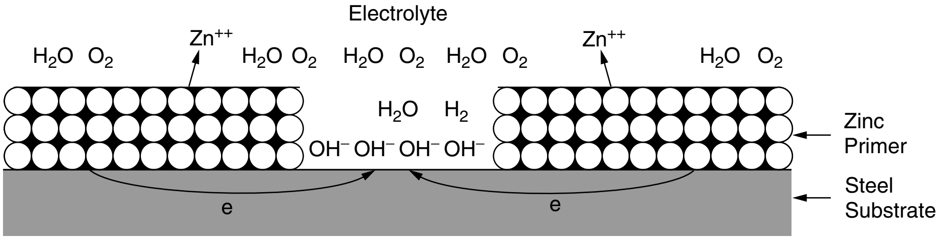

FIGURE 102.6 Fundamentals of zinc-rich protection. The presence of strongly electronegative zinc-pigmented coating short-circuits all local cell activity on steel. The steel becomes totally cathodic to the zinc anode. The zinc corrodes, but the steel will not corrode even at bare spots. It is mandatory that the zinc coating be in electrical contact with the steel surface; therefore, the steel must be stripped of all contamination.

generally used for light to moderate duty atmospheric service, although they may be part of relatively high performance systems such as automotive primers, aircraft coatings, and coil coating primers. They are generally not favored for long-term freshwater immersion service, however, or for continuous use under high-temperature, highly humid conditions.

The formulation of inhibitive metal primer is considered in several texts and papers.[8,9,11,22,23]

102.2.4 Zinc-Rich Coatings

Zinc-rich coatings contain high loadings of zinc dust as a pigment and serve to prevent corrosion galvanically by acting as the anode of an electrochemical cell of which the steel substrate is the cathode (Figure 102.6).[17,24] All local cell activity on the steel is thus overridden by the electrically proximate anodic primer, which itself corrodes sacrificially to protect the steel. Eventually the zinc surface becomes partially polarized with zinc corrosion product, and protection shifts to a quasi-barrier mechanism, as the corrosion product seals the porosities of the highly pigmented zinc film surface. Where organic binders (epoxies, high-styrene systems, moisture curing urethanes, etc.) are used, PVC/CPVC ratios must necessarily be adjusted to unity (or a little higher) in order to maintain the required conductivity (from pigment particle to pigment particle within the film and from pigment particle to substrate). This precept gives rise to exacting requirements in formulation, preapplication homogenization of the primer, and application itself. Too low a PVC will preclude cathodic protection; too high a PVC will result in weak films with poor mechanicals.[25]

Inorganic binders such as alkaline silicates and alkyl silicates rely on chemical reaction of the binder with the zinc atoms on the surface of the zinc dust pigment, and probably the steel substrate also (during application and curing) to produce a wholly continuous, chemically bound, inorganic matrix of zinc silicate.[17,26] While PVC/CPVC levels are somewhat less critical, high levels of zinc are still necessary to provide good cathodic protection over the long term. Although these films are more porous than are the organic zinc-rich systems, again the presence of water within the primer, even against the metal surface, is not threatening to steel, for zinc corrosion is its only consequence. As long as there remains sufficient zinc within the film, all oxidation must occur only within the film itself. Eventually zinc corrosion product packs the porosities and seals the film off as was the case with the surface of the organic zinc-rich film.

Zinc-rich primers are widely employed as nontopcoated systems in environments where the zinc corrosion product is not easily dissolved (i.e., in neutral environments). In such applications, inorganic zinc primers have protected steel for half a century and more. In other systems, especially where environments are either highly acidic or highly alkaline, and therefore reactive with the metal, both organic and inorganic zinc-rich primers are recoated with barrier topcoats (epoxies, vinyls, chlorinated rubbers, and urethanes) for additional protection.

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