

Unified Model for the Degradation of Organic Coatings on Steel in a Neutral Electrolyte

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INTRODUCTION

Organic coatings are widely used to protect metals against corrosion. Despite improvements in coating technologies, problems continue to exist in long-term protection of metals from their environments. Considerable research on the degradation of coated metals has been performed and significant advances in understanding the mechanisms and modes of failure of these materials when exposed to a corrosive environment have been made.¹⁻⁸ However, there has been little work to quantitatively describe the degradation processes and to predict the performance of a coating/metal system during service. One of the main reasons for the lack of a comprehensive theoretical framework for understanding and predicting corrosion protection by a coating is the complexity of the coating/metal system and the many factors that affect the performance and service life of a coating system. For example, besides the physical and chemical properties of the coating, the substrate, and the coating/substrate interface, a coating system may contain inhomogeneities, both in the coatings and at the coating/substrate interface. These factors influence the transport of corrosive species through the coating and along the coating/substrate interface, as well as the degradation processes at the interface.

If the effectiveness of protective coatings is to be increased through development of improved selection and evaluation criteria, it is essential to develop improved methods for quantifying the degradation and predicting the service life of a coated metal. This paper presents a unified model, containing both conceptual and mathematical components, for the degradation of a protective coating on a steel substrate exposed to a neutral electrolyte. The unified model is based on theoretical and experimental studies from our laboratory as well as on current understanding of the degradation process. This model can provide a useful tool for better predicting the performance and service life of organic protective coatings.

DEGRADATION MODES OF ORGANIC-COATED STEEL IN NEUTRAL ELECTROLYTES

For a coating system containing a scribe mark or a large defect exposed to a neutral electrolyte, e.g., NaCl, the degradation

A unified model is presented for the degradation of an organic protective coating on a steel substrate exposed to a neutral electrolytic environment. This model is based on theoretical and experimental studies from our laboratory and on current understanding of the degradation process. The assumptions of the model are based on the concept that degradation of a coating/steel system occurs following the transport of ions through conductive pathways, which are presumably formed by an attack by water in the "hydrophylic," low-molecular-weight/low-cross-linked regions, followed by the connections of these regions. Models for the blistering and delamination resulting from corrosion processes are based on the diffusion of cations along the coating/steel interface from the defects to cathodic sites under the coatings. The resulting equations are solved to predict ion fluxes and concentration profiles along the interface and within blisters. Model variables include blister size, distance between blister and defect, ion diffusivity, and potential gradients. Experimental results agree well with theoretical predictions.

phenomenon is generally understood.⁵⁻¹² Corrosion takes place at the defects while delamination or blisters appear adjacent to the defects (Figure 1a). This degradation phenomenon, which is the most severe among the failure modes of organic-coated steel, is often observed on metal objects with damaged coatings, e.g., a dented car fender or a scratch on the outside wall of a building. The loss of adhesion in the vicinity of large defects is generally known as cathodic delamination and blistering because it is due to the half cell cathodic reaction of the corrosion process. In an alkaline electrolyte, cathodic delami-

Presented at the 73rd Annual Meeting of the Federation of Societies for Coatings Technology, on October 10, 1995, in St. Louis, MO.

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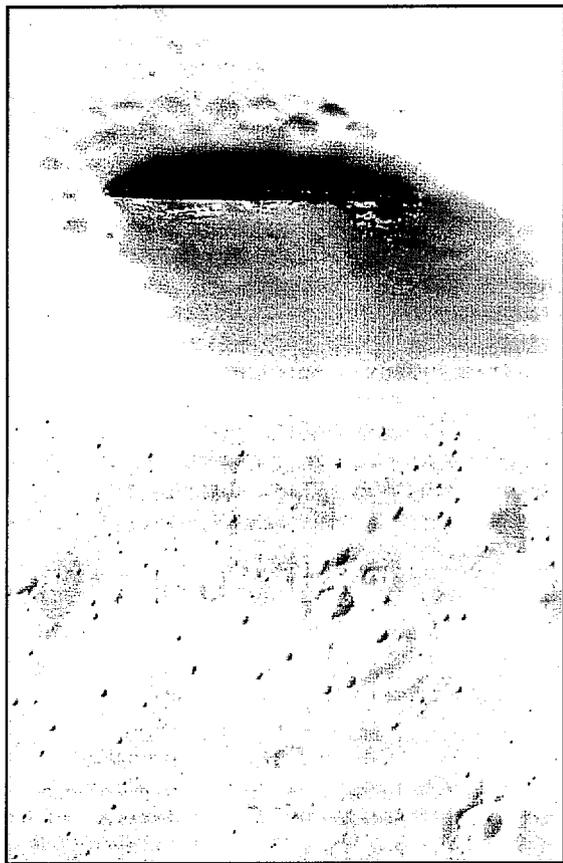


Figure 1—Degradation of coated steel panels in a neutral electrolyte: (a) with scribe mark, and (b) without apparent initial defects.

nation also occurs near a scribe; however, corrosion does not occur at the defect site (as in a neutral electrolyte) but under the coating adjacent to the scribe mark.¹³ Although the model presented here is generally applicable, this paper does not discuss further the degradation process in an alkaline electrolyte.

For coated steel panels containing pores, pinholes, or small-sized defects exposed to a neutral electrolyte, corrosion also occurs at the defects, and cathodic delamination takes place around the defects.^{3,8} However, cathodic blistering at the pores has also been observed.^{14,15} In this case, the anodic reactions take place on the metal surface below the pore bordered by circular cathodic sites. The pore, which contains corrosion products, is at the center top of the blisters. Funke suggested that corrosion products, which act as a semipermeable membrane, block the pores and cause increased water uptake around the defective areas. Martin et al.¹⁶ also observed cathodic blistering (Figure 1b) with a small corroded area near the blister center of alkyd-coated steel panels containing no apparent coating defects (undetected by a holiday detector), but subjected to constant immersion or cyclic wet-dry exposure to a NaCl solution. They noted that it took a much longer time for blisters to occur on these panels than on those containing a scribe mark. It is suspected that some types of defects must have been formed in the coatings of these panels during exposure because it has been shown that the degradation of organic-coated steel occurs only at the defects, even for coating films as thin as a monolayer.¹⁷ These results

suggest that organic-coated steel panels containing no apparent defects exposed to a neutral electrolyte follow the same degradation processes as specimens containing small-sized defects.

Although the degradation modes and mechanisms of organic-coated steel immersed in a neutral electrolyte are generally known, several critical questions remain unanswered. For example, do both cathodic delamination and blistering appear on the same coating/substrate system or does each mode occur on a certain type of the coatings? If the latter is true, then what are the fundamental properties of the coatings that dictate the cathodic failure mode, e.g., moduli, wet T_g ? Another question that needs to be addressed is whether cathodic blisters are formed randomly or are associated with certain sites at the coating/substrate interface, e.g., interfacial microvoids, defects in substrate surface structure? Answers to these questions would provide a clearer understanding of the corrosion and protection of organic coatings on metal.

UNIFIED MODEL FOR DEGRADATION OF ORGANIC-COATED STEEL

Conceptual Model

Based on the evidence presented in the preceding section, we believe the degradation of a typical organic-coated steel panel containing no apparent defects (good coating) exposed to a neutral electrolyte solution follows the steps (indicated by circled numbers in Figure 2) depicted graphically in Figure 2b. For completeness, a conceptual model for the degradation of a coated steel panel containing a large defect or a scribe mark is illustrated in Figure 2a; except for the events and the phenomena taking place away from the scribe, the processes at the scribe mark are similar to those proposed by Dickie and Smith.⁵

Formation of Conductive Pathways

One group of researchers has proposed that the formation of conductive pathways (step 1) that allows ions to reach the metal surface is the first step in the degradation of a good coating or a multilayer coating on a steel substrate exposed to a neutral electrolyte;^{3,18,19} while another school of thought believed that water sorption in the coating is the first step.²⁰⁻²² A linkage between these two phenomena, i.e., water sorption and conductive pathway formation, would provide a unified view of the initial step in the degradation of a defect-free, organic protective coating.

Actually, these two views are not different from one another if conductive pathway formation is the consequence of the water uptake in the coatings. There are several pieces of information to support the linkage between these two phenomena. The strongest evidence is from the findings of numerous studies indicating that coating films inherently contain microscopic regions that take up large amounts of water and have low ion resistivity.²³⁻²⁸ Further, corrosion spots on the substrate have been found to be directly related to these regions.^{23,28} Additional evidence is from scanning electron microscopy (SEM) studies, which clearly showed that water does not diffuse into the film uniformly but in a dense layer along the boundaries of the polymer structure units, followed by penetration into the structures themselves.²⁹ Such diffusion leads to destruction of the molecular network structure

and the protective efficiency of the coating. Phase-contrast microscopy results also revealed that the water droplets in the low ionic-resistant coatings are finely dispersed, while the water droplets in the high-resistant films are isolated.²⁰ Mayne postulated that the transport of ions through isolated droplets is more difficult than through the finely dispersed water medium, and provided an explanation for the resistivity difference between the two coatings. Further, the induction period before cathodic blistering occurred on a coated panel containing no apparent defects has been found substantially longer than that containing a scribe mark.¹⁶ The results presented strongly support the notion that conductive pathway formation is a direct result of the water uptake in the coatings. Thus, for good or multilayer coatings, water uptake is the first step of the degradation process; this process causes the opening of conductive pathways in the coatings, allowing ions to reach the substrate surface. The exposure time required for this process to occur is expected to be a function of the coating type.

We believe that the formation of conductive pathways in an organic coating during the water uptake period is due to an attack by water in the "hydrophylic" regions in the film, followed by the interconnections of these regions. The presence of macroscopic defects such as craters and pinholes,^{30,31} air bubble inclusions,³² poor adhesion between pigment and binder,³³ or mechanical damages in the coatings would accelerate the pathway connections. Swelling, stress relaxation, and conformational changes in the coatings during exposure may all contribute to the formation and enlargements of such pathways.

Hydrophylic regions are regions that contain low-molecular-weight/low-crosslinked (LMW/LC) materials. They take up a large amount of water, have a low resistance to ion transport, and are susceptible to water attack, e.g., hydrolysis and dissolution. The inherent presence of inhomogeneities and phase separation in a polymer or coating film is well documented. Indeed, this property is the main cause of the deviations between experimental data and the theory of the equilibrium formation of crosslinked polymers, which leads to the introduction of empirical parameters into rubber elasticity laws. Karyakina and Kuzmak²⁹ have discussed in detail coating heterogeneity and concluded that organic coatings should be considered as consisting of microgels connected via a spacial network. Corti et al.²⁸ briefly reviewed the inhomogeneous nature of paint films and believed that this property is intrinsic in these materials. Funke^{34,35} has studied the effects of various processes on the phase separation of paint films, especially during the curing and drying processes.

The presence of low-molecular-weight (LMW) regions in coating films has been demonstrated by electron and light microscopy studies.^{36,37} Films made of epoxy, phenolic and phthalate resins were observed to consist of micelles or granules of high-density segments separated by narrow boundary regions of LMW material. At the film/substrate interface, the LMW material may exist as a thin continuous film or as channels between micelles, thereby providing pathways for the easy entry of water to the interface.³⁸ Bascom surmised that inhomogeneity in coating films is due to a phase separation during film formation. As the high-density segments approach one another from random initiating sites, they are unable to merge into a homogeneous structure. Instead, for chemically cured coatings the polymerization is terminated

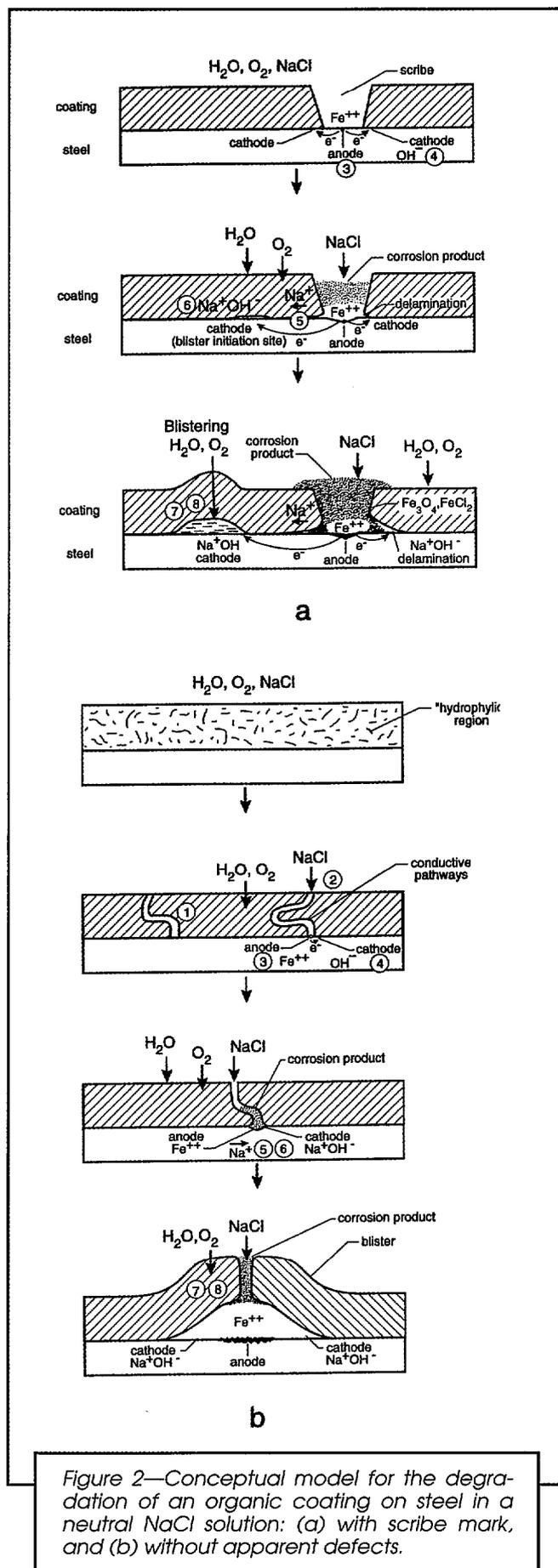


Figure 2—Conceptual model for the degradation of an organic coating on steel in a neutral NaCl solution: (a) with scribe mark, and (b) without apparent defects.

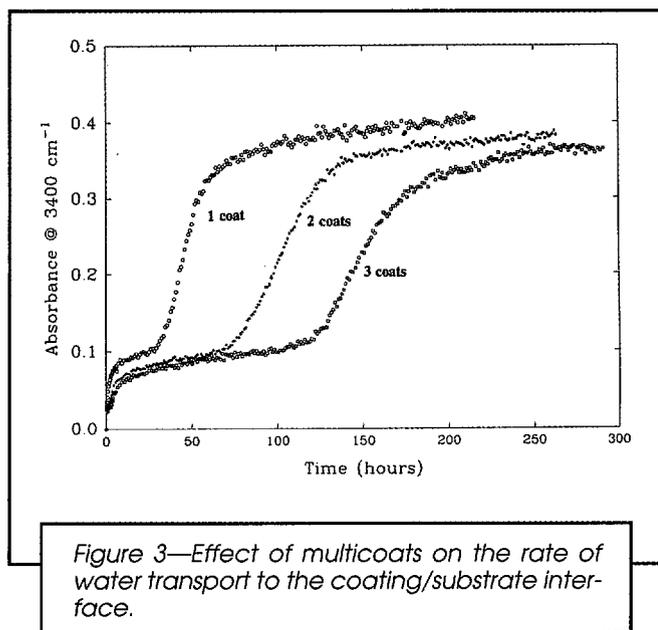


Figure 3—Effect of multicoats on the rate of water transport to the coating/substrate interface.

leaving the unreacted or partially reacted materials at the periphery.

Using D.C. resistance and microhardness measurements, Mayne and coworkers²³⁻²⁶ have identified a “conducting polymer phase,” which they designated as D area, in a variety of coating films. D areas, whose diameters range between 75 and 250 μm , constitute only a small fraction of the film and have physical and chemical properties completely different from the rest of the film. Fernandez-Prini and Corti^{27,28} have also observed an extensive degree of heterogeneity in epoxy/polyamide coal-tar films. Some regions in these films behave similarly to the D type described by Mayne. Mills and Mayne²³ postulated that D areas are formed by partially polymerized or “dead” molecules, which are present in the resin before casting. During drying, these molecules congregate, form micelles, and due to low functionality, do not crosslink to the same extent as the rest of the film. Thus, it appears that the low crosslinked (LC), D type areas observed by Mayne resemble the microscopically observed, low-molecular-weight

(LMW) regions described by Bascom.³⁸ Both of these descriptions are consistent with SEM observation of Karyakina and Kuzmak,²⁹ which showed that the transport of water through a coating film is along the boundaries around the polymer network units.

Corti et al.²⁸ have observed that the water sorption and transport characteristics of the D areas are typical for a hydrophilic, ion-exchange membrane. This type of material takes up about 45-75% water and has ion diffusion coefficient in the 10^{-5} cm^2/s range. This means that the LMW/LC (D type) regions would take up much more water and have much lower ionic resistances than the rest of the film. Typical organic coatings take up approximately 2-5% water and have ion diffusion coefficients in the 10^{-10} - 10^{-13} cm^2/s range.^{6,39} Further, the transport of ions in the LMW/LC regions probably follows the Cohen-Turnbull⁴⁰ mechanism, whereby the rate determining process for diffusion is the thermal density fluctuations of the mobile water molecules sorbed within the polymer. This transport mechanism is strongly dependent on the amount of water that has been taken up. The LMW/LC, high water uptake, low-ionic resistance regions (D type) in a coating film are referred to hereafter as the hydrophilic regions.

The assumption that conductive pathway opening is due to chemical activation by water is consistent with the observations of several studies. Kittelberger and Elm⁴¹ have attributed a much higher diffusion rate of NaCl in linseed oil films than in films of other resins, e.g., phenolic or alkyd, to the large concentrations of hydrolyzable materials in the linseed oil. Mayne²⁰ proposed that the easier passage of ions through linseed oil films relative to other coating films is due to a finely dispersed distribution of water in the former, as indicated earlier. Water soxhlet extraction studies by Walker⁴² also showed that long-oil alkyd and short-oil epoxy ester coatings lose about 4-5% water-soluble materials. Further, hydrolysis has been observed as a common mode of degradation of a variety of coatings and resins exposed to water and high relative humidities, both in the presence and absence of sunlight.⁴³⁻⁴⁹ Hydrolysis by water has been reported as the main cause of microcavitation, microcracking, irreversible mechanical loss, and etching (acid) of polymer and coating

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films.^{43,46,47,49} It should be mentioned that both ester and amide linkages, which are commonly present in coatings and related materials, are susceptible to hydrolysis reactions and are strongly catalyzed by an acid or a base.

Interestingly, several studies have linked coating degradation directly to the electrolytes. For example, Leidheiser et al.⁵⁰ and Tait⁵¹ suggested that cations of the electrolytes cause morphological changes in coatings leading to conductive pathways through the coatings. Walter¹⁹ also postulated that electrolyte solution ingresses permanently damage the film and that this damage increases with time. Cations generally do not directly attack a neutral, polymeric molecule, e.g., an ester, unless cations are of a strong base, e.g., NaOH, which is formed in the cathodic regions. In this case, the strong nucleophile, OH⁻, of the base adds readily to the carbonyl carbon of the ester following the nucleophilic addition-elimination mechanism.⁵² This would accelerate hydrolysis reactions with the formation of the salt of the cation (e.g., -COO-Na⁺). However, Leidheiser et al.⁵⁰ has provided evidence to show that corrosion could not cause the damage. Thus, it is more likely that cations are involved in the degradation process through the salt formation with the hydrolysis products in the hydrophylic regions, and not by reacting directly with the polymer chains. The resulting salts (soaps) are not only much more water soluble than the corresponding esters but are also capable of solubilizing nonpolar organic substances.

Based on the previously mentioned evidences and discussion, it is concluded that water attack, e.g., hydrolysis and dissolution, in the LMW/LC, hydrophylic regions causes a loss of coating material in these regions. This is probably the primary process leading to the formation and opening of conductive pathways in organic coating films exposed to electrolytes. This hypothesis is in good agreement with the observations by Mayne and Mills^{23,26} and Fernandez-Prini and Corti^{27,28} that the loss of coating protective capability starts in the low crosslinked, low resistant, D areas and that corrosion spots on the steel surfaces under coatings correspond directly to these areas. For poor coatings, some macroscopic defects may be large and continuous through the film, providing pathways for electrolytes to reach the interface within short exposure times. For good or multicoat films, defects may not be continuous or large enough for ions to migrate through. For these coatings, prolonged or repeated exposure is required for the formation and connection of openings in the hydrophylic regions. Since the percentage of hydrophylic areas in a film is small, the chance of one hydrophylic area overlapping another hydrophylic area in succeeding layers is low. Thus, a multicoat film is a more effective protective coating than a single coat of the same thickness, consistent with general practice.

The opening of new and/or enlargements of existing pathways during exposure has been proposed by several workers. Kendig and Leidheiser¹⁸ have related changes in electrical properties to the formation of pathways and indicated that ions initially penetrate to random depths at numerous sites; with time, paths of complete penetration develop. Similarly, based on evidence from potential, impedance, and degradation measurements, Walter¹⁹ postulated that there may be a few continuous pathways at first, but many pathways will develop with time. He also showed that pathway area increased with exposure time in solution. Skerry and Eden⁵³ estimated that the apparent area of the pores increased from

an initial 0.6 μm^2 to 6700 μm^2 per cm^2 of the coatings after 100 days exposure to the 0.6 mol/L NaCl solution. Another example of the increasing number of pathways with exposure is from a study of powder epoxy coatings on reinforced steel bars, showing that the number of holidays detected after 24 hr exposure to a 0.6 mol/L NaCl solution was higher than when initially inspected.⁵⁴

Nguyen et al.⁵⁵ have provided spectroscopic evidence to support the proposal that the transport of materials in coating films is through the interconnections of interrupted pathways; Figure 3 presents their results. These curves are plots of the Fourier transform infrared intensity corresponding to the amounts of water at the coating/substrate interface⁵⁶ for one, two, and three coats, respectively, of a water-reducible epoxy coating on a germanium substrate. The thickness of the one-, two-, and three-coat films were 141, 208, and 242 μm , respectively. The results clearly showed that the rate of water entering the coating/substrate interface (the slope) decreased with increasing number of coats. Thickness differences among the specimens cannot explain these results because film thickness generally only affects the time required for water from the outside to reach the coating/substrate interface (time-lag).

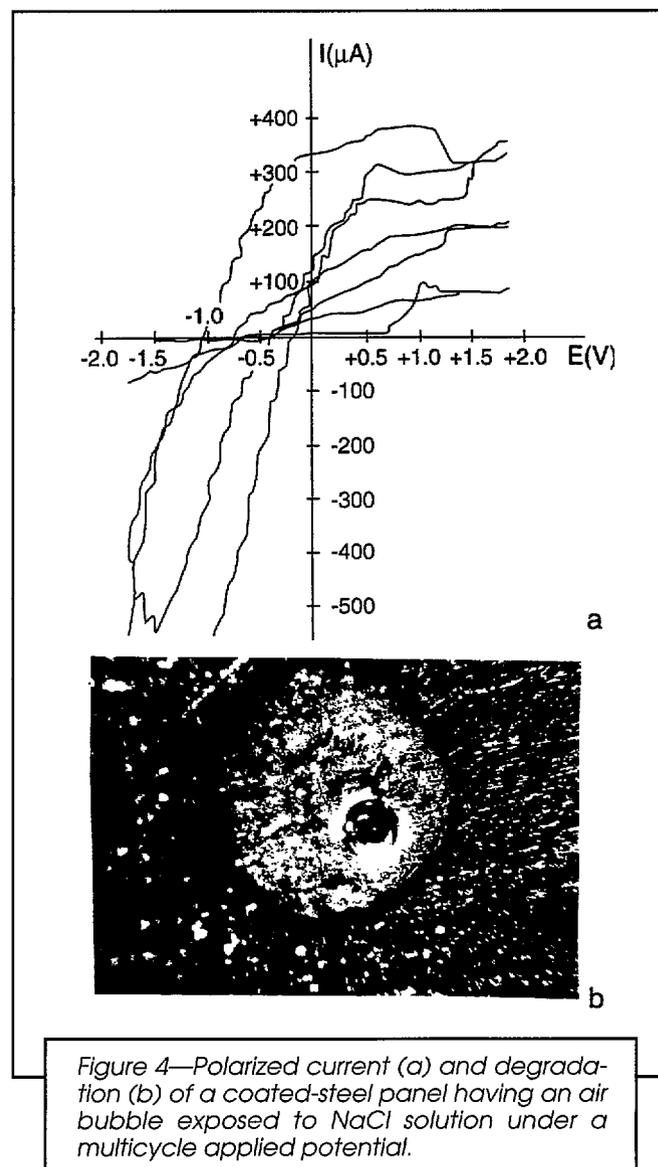


Figure 4—Polarized current (a) and degradation (b) of a coated-steel panel having an air bubble exposed to NaCl solution under a multicycle applied potential.

The results suggest that increasing the number of coats increases the tortuosity of the transport pathways in the coatings.

Transport of Corrosive Species to the Metal Surface

Following the pathway formation, the next step in the degradation of coated steel is the transport (step 2) of water, oxygen, and ions from the environment to the metal surface. However, typical organic films are permeable to water and oxygen so that the transport of these materials is not rate controlling.^{1,5,7} Further, it has been established that the loss of barrier properties and the development of conductive pathways in an organic-coated metal normally coincide with the initiation of corrosion processes at the metal surface. Based on experimental evidence, Walter^{2,19} suggested that the ingress of ions through the coating is the primary process responsible for the degradation of an epoxy primer/topcoat system. Mayne²⁰ shared this view for low-resistant coatings; but for high-resistant coatings, he believed the transport of ions is secondary to water uptake. Kittelberger and Elm⁴¹ reported a linear relationship between the rate of diffusion of NaCl and the reciprocal of the film resistance. Since coating resistivity is directly correlated with corrosion,⁵⁷ this result suggests that ion transport through the coatings may be the primary process in the degradation for certain types of coatings.

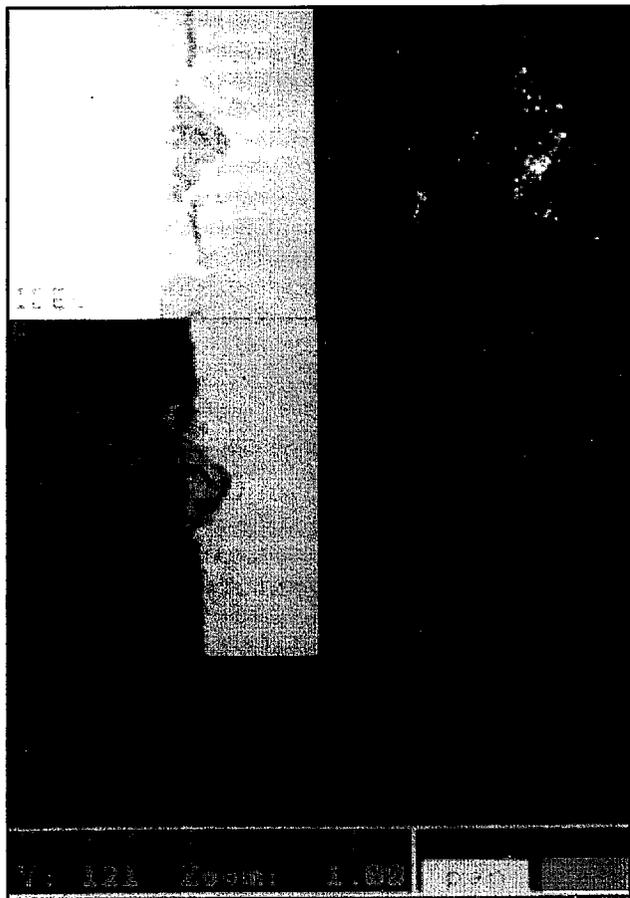


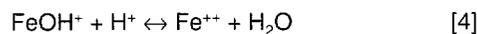
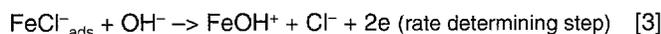
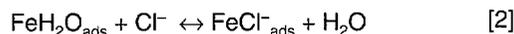
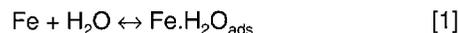
Figure 5—SEM image and distributions of Cl and Fe at the scribe mark in an organic-coated steel panel exposed to a 0.51 NaCl mol/L solution for 168 hr.

Regardless of the rate controlling step, the transport of ions from the environment to the metal surface is through discrete, least-resistant, conductive pathways in the coatings.^{3,18,19,58} This view is supported by the fact that the solubility of ions in a polymer matrix is extremely low, on the order of 10^{-8} mol/L in equilibrium with one molar electrolyte.⁷ Ion transport through conductive pathways is in agreement with the practical observation that corrosion of coated metals occurs on the bare metal area at the base of defects in the coatings or at mechanical damage sites. It is also consistent with the impedance equivalent circuit models, which generally consist of the coating capacitance shorted by a resistive element, due to the formation of ionically conducting pathways through the coatings.^{58,59}

Figure 4 provided both direct and indirect evidence to support the assumption that the transport of ions is through the lowest-resistance pathways. The specimen was a 60 μm thick, clear acrylic coating on a steel substrate containing one air bubble, which was enclosed in a corrosion cell containing a 0.51 mol/L NaCl solution. A multicyclic potential between -1.8V and $+1.8\text{V}$ was scanned across the specimen at a rate of 0.1V per second. The polarization currents (Figure 4a) rose rapidly within five minutes of applying the potential. No current was detected for specimens containing no bubbles or other defects, even after scanning for three hours under the same cyclic potentials. For the specimen shown in Figure 4, there was no evidence of corrosion inside or outside the bubble during the five-minute scanning. However, corrosion was observed upon further immersion as seen in Figure 4b (17.5X). Brownish corrosion products were visibly observed inside, and a light-color ring around the air bubble appeared after approximately one hour of exposure. The corrosion products in the bubble became voluminous and the area within the surrounding ring progressively expanded with exposure. Other examples with minor defects in the coatings also showed similar phenomena.⁶⁰ These results indicated that the transport of ions to the metal surface was through the least-resistant pathways and that corrosion starts at the base of the pathways. It should be emphasized that the cyclic applied potential caused very little, if any, physical damage to the coatings.^{60,61}

Degradation at the Defect or Pathway

Once conductive pathways are established and ions have reached the metal surface, the degradation of a coating system without apparent defects is believed to be the same as that containing a small defect, as indicated earlier. A corrosion cell is set up and near the defects or pathways. The anodes develop (step 3) on the bare steel at the bases of the pathways,^{3,6,7} where corrosion reactions take place following several steps⁶²:

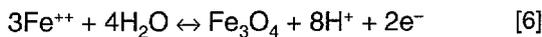


The net result is the production of electrons and Fe^{2+} ions in solution. The rate of formation of the first oxidized layer in

the presence of Cl^- ions has been found to be several orders of magnitude higher than that in water alone.⁶³ Subsequent oxidation and hydrolysis result in a decrease of the pH and formation of a complex mixture of hydrated iron oxides (rust) at the defects:



For coatings containing large defects or scribe marks, reactions [1] to [5] also occur at the bare steel of the coated panels (Figure 2a). In this case, anodes and cathodes may initially develop in the proximity.^{5,9} As corrosion products form and concentration gradients of corrosive species are established, the reaction sites separate and localize. Continued exposure leads to an increase of this separation. As corrosion progresses, the rust layers at the defects become a barrier to the transport of oxygen. According to Pourbaix,⁶⁴ the formation of Fe_3O_4 products is thermodynamically favored (large negative enthalpy of formation) in this environment, following the reaction:



In the presence of chloride ions, HCl can form and aggressively promote the dissolution of iron at the defects, resulting in an increase of Cl^- ion migration. The effect is a rapidly accelerating, or autocatalytic, process at the bottom of the defect. With the buildup of excess Fe^{2+} and H^+ ions within the confined local electrolytes, negatively charged ions are required to preserve charge neutrality. However, for coated metals, mobile negative charged species are limited. The cathodically produced OH^- ions are captured near their production sites by the organic coating, as evidenced by the high pH at the delamination fronts.⁶⁵ On the other hand, Cl^- ions are abundant in the bulk solution and migrate into these locations to preserve electrical neutrality. The result is an increased local concentration of ferrous chloride following the reaction^{64,66}:



Thus, the products in the solution under the rust layers at the bottom of a scribe mark probably contain mostly $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and Fe_3O_4 (Figure 2a), similar to those observed for localized corrosion of uncoated iron. Oxidized corrosion products are anion-selective,⁶⁷ allowing Cl^- ions to continuously permeate through the rust layers and reach the metal surface. Sato⁶⁷ postulated that water probably continuously flows into the anodic sites under the rust layers by an electro-osmosis process, which accompanies the permeation of Cl^- ions.

Reaction [7] accounts for the presence of large amounts of chloride at corroded sites, as illustrated in Figure 5. This figure shows a SEM image and the distribution of Cl, Fe, and Zn (Zn is from the pigment in the coating) elements at a scribe mark of an alkyd primer/topcoat on a steel panel immersed in a 0.51 mol/L NaCl solution for 168 hr. Although some corrosion products were lost during specimen preparation, the large concentrations of Cl deposited at the bottom of the scribe and around the Fe corrosion products are clearly seen in the Cl map. These results support the suggestion by Ritter and Rodriguez⁹ that the corrosion process under the corrosion products at a scribe mark is similar to that for localized corrosion of uncoated iron. The fluid within the crevices of uncoated iron exposed to neutral NaCl solutions is acidic and contains a 3-10 times higher concentration of Cl^- ions than

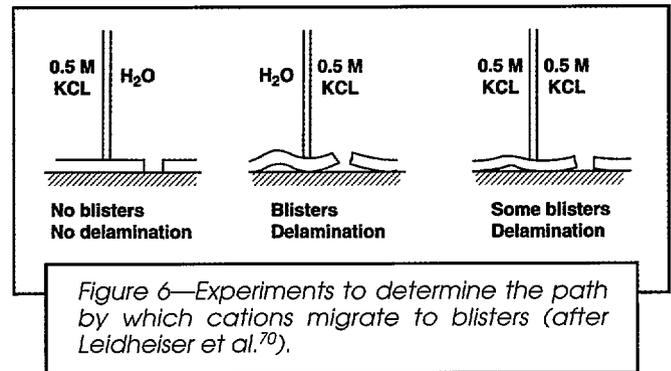


Figure 6—Experiments to determine the path by which cations migrate to blisters (after Leidheiser et al.⁷⁰).

that of the bulk solution.⁶⁸ For coated iron, Ritter and Rodriguez⁹ reported a 3-4 times higher Cl^- ion concentration in the anode formed at the coating/iron interface than in the bulk after one week exposure to a 0.05 mol/L NaCl. Nguyen and Lin⁶⁹ also found a 10-fold higher Cl^- concentration in a corroded, anodic blister formed on an alkyd-coated steel panel exposed for six months to a 0.51 mol/L NaCl solution.

Degradation Around the Defect or Pathway

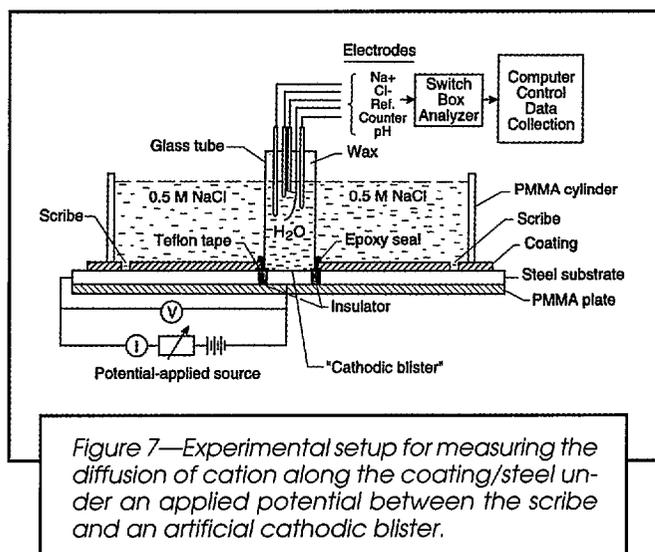
Under the coating near defects, cathodes are formed (step 4). The primary corrosion reaction is oxygen reduction^{3,5,7,70}:



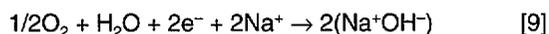
Every electron produced by the anodic reactions (reaction [3]) is consumed by the cathodic reaction. Thus, there is a strong electrochemical coupling between the defect (anode) and the cathodic sites under the coating. First, the transport of electrons results in a flow of a galvanic current (corrosion current) between the defect and the local cathodes. This flow requires cations transport between the two sites.⁷ The current is high if the ion conductivity between the defect and cathodes is high, which occurs, e.g., when the coating/substrate interfacial area between the anodes and cathodes has been delaminated or blistered.⁷¹ Preventing the flow of the corrosion current would halt the corrosion of organic-coated metals.

There is also a substantial potential gradient between the defect and an associated cathode at the coating/substrate interface. This potential has been found as the driving force for the cathodic delamination of organic-coated steel in electrolytes.^{7,72} Lowering this potential gradient would minimize the cathodic delamination and blistering.^{72,73} Using a Kelvinprobe technique, Stratmann and coworkers^{7,17,72} have measured the potential gradients between a defect and a random location at the coating/metal interface surrounding the defect. For coated iron exposed to an electrolyte, they range from +0.05 to $-0.4V_{\text{SHE}}$, with more negative voltages at locations closer to the defect. The measurement of this potential has provided a good way to nondestructively monitor the growth of the cathodic regions under coatings. The intact coating/metal interface is characterized by positive potentials, whereas a delaminated area is recognized by the negative potential plateau. The delamination front is identified by the transition between negative and positive potentials.

The regions underneath the coatings where cathodic reactions occur serve as the initiation sites for delamination or blistering. The pH at the cathodic delamination areas and



in cathodic blisters is high. This has been proven by the strong violet coloration, either from a transparent coating containing a phenolphthalein pH indicator⁷ or after spraying the same indicator over the delaminated area. Ritter and Kruger⁶⁵ have recorded pH values as high as 14 at the front of the delamination. The strong alkalinity at the cathodic sites has been attributed to the migration of cations (step 5) from the environment to the cathodic sites, neutralizing the negative charge of the hydroxide ions following the reaction^{6,7,13,73}:



The presence of Na in the cathodic delaminated areas has been verified by surface analytical techniques.^{7,74}

In the absence of an applied potential, the transport of Na⁺ ions to the cathodic sites appears to be along the coating/metal interface via defects, pores, or conductive pathways in the coatings, as demonstrated experimentally by Leidheiser et al.⁷⁰ (Figure 6). They found that cathodic blisters developed only if pores or similar coating defects extending to the metal surface were exposed to electrolytes. These results were confirmed by Funke.⁶ Based on evidence from Kelvinprobe measurements, Stratmann et al.⁷ went further to suggest that not only cation diffuses along the coating/metal interface from the defects to the cathodic sites but also this transport process is the rate controlling step of the cathodic delamination phenomenon. Nguyen and co-workers^{73,75,76} have assumed the same transport process as the rate determining step in their model for the cathodic blistering process of coated steel in neutral electrolytes. They further predicted that the cation flux into the cathodic blisters is almost a linear function of the potential gradient between the defect and cathodic sites.

For cathodic delamination, the alkalinity of the solution at the delamination front has been proposed as the cause for the disbondment (step 6) of a coating from a steel substrate.^{3,11,70,78} However, the rate of delamination is a function of many factors, including potential difference between the defect and local cathodes, applied potential across a coated panel, type and concentration of cations, type of coating and metal, metal surface pretreatment, temperature, and oxygen concentration.^{4,7,39,70,72} Three possible mechanisms have been advocated for the cathodic delamination of a coating: dissolution

of the oxide layer,^{65,70} alkaline hydrolysis of polymer,¹¹ and interfacial failure.⁷⁷ In some coating/metal systems, more than one of these mechanisms is involved, either simultaneously or in stages.⁷⁸ Recent developments have allowed the cathodic delamination rate to be measured more precisely, either nondestructively^{7,72} or destructively.¹³

For cathodic blistering, the alkalinity of the cathodic reaction products is also believed to be responsible for the interfacial disbondment at the cathodic sites. However, the high water solubility of the product from reaction [9] is probably responsible for blister formation.^{12,73} This alkaline material reduces the water activity and creates an osmotic pressure gradient (step 7) between the environment and the coating/steel interface at the blisters. This osmotic pressure gradient is probably the principle mechanism for the growth (step 8) of cathodic blisters.^{6,12,14,73,79,80} Alternately, Martin et al.¹⁶ suggested mechanical stress may be the main cause for growth of cathodic blisters.

Based on this conceptual model, the steps (circled numbers in Figure 2b) involved in the degradation of an organic-coated steel panel containing no apparent defects exposed to a neutral NaCl electrolyte may be summarized as in the following:

- (1) Conductive pathways develop by water attack in the hydrophylic regions of the film, followed by interconnection of these regions; macroscopic defects (in the coatings) accelerate this process;
- (2) Ions migrate through conductive pathways to the metal surface;
- (3) Anodes develop on the metal surface at the base of the pathways;
- (4) Cathodic contacts develop under the coating at the periphery of the pathways;
- (5) Sodium ions migrate along the coating/metal interface from the defect to the cathodic sites to neutralize the hydroxyl ions; this transport process is the rate determining step;
- (6) Alkalinity of NaOH product at cathodic sites causes disbondment (cathodic delamination);
- (7) Hygroscopic NaOH materials at cathodic sites produce a water activity difference between the environment and interface, setting up an osmotic pressure gradient; water is driven to cathodic sites through the coatings by an osmotic pressure gradient; and
- (8) For some coatings, blisters develop, enlarge (probably facilitated by mechanical stresses), and eventually coalesce, resulting in total delamination.

MATHEMATICAL MODEL

Transport of Ions to Metal Surface

As indicated earlier, once conductive pathways are established, the next step in the degradation of a good coating/steel system in a neutral electrolytic environment is the transport of ions through the pathways to the substrate surface. Our models of the transport through these types of coatings are based on mass diffusion through an impermeable slab punctured by tortuous transmembrane pores. The physics of this

transport is best illustrated in the simplest example: a planar membrane of thickness, l , containing pathways (pores) having contour length, δ' , initially free of diffusive species, with a steady concentration difference c_0 across the two faces. The pore-average transient flux through an imperfect, amorphous membrane is given by⁸¹:

$$\langle F(t, l) \rangle = \int_0^\infty dx P(x) F(t, \sqrt{x}l) \quad (1)$$

and the steady-state flux is then given by:

$$\langle F(0, l) \rangle = \frac{Dc_0}{l} \int_0^\infty dx x^{-1/2} P(x) \quad (2)$$

where $P(x)$ is the pore length probability function, $F(t, \sqrt{x}l)$ is the Fickian diffusive flux through a set of pores having the contour length $\delta' = x^{1/2}l$, and D is the diffusion coefficient in the pores. $P(x)$ in an amorphous membrane has been described and calculated by Hubbard et al.⁸¹ in which pores were constructed by finite variance, continuous random walk algorithms. Simulation and analytical results for the length distribution of pores in 1-D, 2-D, and 3-D (D for dimension) for both asymmetric and symmetric membranes have been obtained. Hubbard et al. deduced explicit forms for $P(x)$ and derived the transient flux for corrosive species through amorphous membranes. For instance, equation (1) has the form (for a 1-D symmetric membrane):

$$\begin{aligned} \langle F(t, l) \rangle = & \frac{-4\pi Dc_0}{l} \sum_{k=0}^{\infty} \sum_{n=1}^{\infty} (-1)^{k+n} \\ & \times \left[4 \left(\frac{n}{2k+1} \right)^2 \frac{Dt}{l^2} \right]^{1/4} \\ & \times K_{1/2} \left[\frac{n(2k+1)\pi^2 (Dt)^{1/2}}{l} \right] \end{aligned} \quad (3)$$

where $K_{1/2}$ is the modified Bessel function of order 1/2. The long-time transient flux is a stretched exponential:

$$\langle F(\tau, l) \rangle = \frac{4\sqrt{\pi} Dc_0}{l} \exp(-\pi^2 \tau^{1/2}) \quad (\tau \rightarrow \infty) \quad (4)$$

where $\tau = Dt/l^2$.

Simulation and numerical results for the fluxes for 1-D, 2-D, and 3-D for symmetric and asymmetric membranes have been presented. The sharpest contrast between mass transport through pore-containing and homogeneous membranes is in the stretched exponential decay [$\exp(-t^\alpha)$, $\alpha = 1/2$] of the long-time transient diffusive flux for a pore-containing membrane versus simple exponential decay [$\exp(-t)$] for a homogeneous membrane. One interesting consequence of mass transport via membranes defect lines, which terminate at a surface, is that a composite membrane consisting of several layers in series should result in a more effective barrier to the diffusion of corrosive species than a single layer of the same overall thickness. This prediction is consistent with the result shown in Figure 3 and with the general practice of protective coatings.

Cathodic Blistering and Delamination

As stated previously, the principle mode of degradation of an organic-coated steel panel with or without defects in the coatings exposed to a neutral electrolyte is cathodic blistering

and delamination. Although the mathematical model was developed for cathodic blistering, it should be equally applicable for cathodic delamination because the governing parameters used in the model are the same for both degradation modes.

The main reaction in the cathodic regions is oxygen reduction with the formation of hydroxide ions (reaction [8]). The basis of the models developed by Nguyen, Hubbard, and McFadden⁷³ to describe this degradation is the transport of cations, especially those of alkali metals such as K, Na, Cs, and Li, along the coating/metal interface to neutralize the OH⁻ ions, which are generated from reaction [8]. The models are based on two assumptions: (1) transport of alkali cations from the defects (anodes) to the blister sites (cathodes) is along the coating/steel interface, and (2) alkali cation transport is the rate controlling step. The first assumption is in accordance with results of Leidheiser⁷⁰ and Funke⁴ for cathodic blistering. Recent experimental data on cathodic delamination by Stratmann et al.⁷ have verified both assumptions. The model is based on a 2-D, radially symmetric diffusion of an ionic species in an annular domain. The transport equation takes the form⁷³:

$$\frac{\partial C'}{\partial t'} = D \frac{1}{r'} \frac{\partial}{\partial r'} \left(r' \frac{\partial C'}{\partial r'} \right) + \mu E \frac{\partial C'}{\partial r'} \quad (5)$$

C' is the cation concentration at any point between the blister and the defect; t' is the exposure time; r' is the distance between the center of the blister and any location on the coated panel between the blister and the defect; D is the effective diffusion coefficient along the coating/steel interface; μ is the average mobility of cations; and E is the strength of the unscreened electric field.

Equation (5) was rewritten in dimensionless units, in terms of distance scale r , time scale t , and concentration scale C :

$$\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} + \frac{p}{r} \frac{\partial C}{\partial r} \quad (6)$$

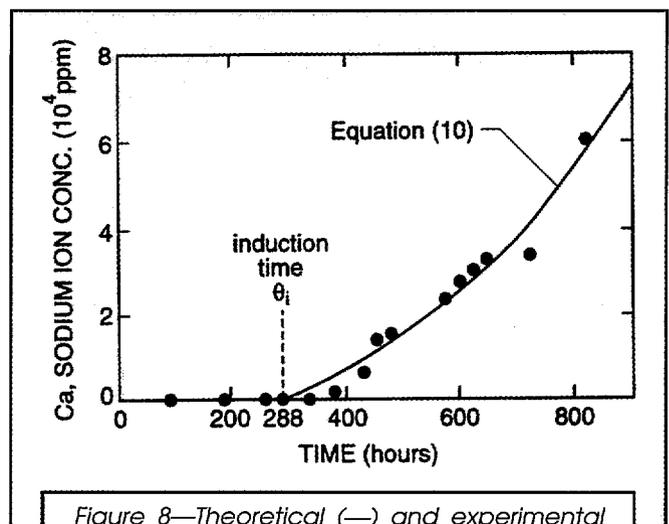


Figure 8—Theoretical (—) and experimental (o) results for Na⁺ ion concentration in a cathodic blister versus time under an applied potential of -0.85V (vs an Ag/AgCl reference electrode) between the scribe and the blister when the scribed area of an epoxy-coated steel panel is exposed to 0.5 mol/L NaCl.

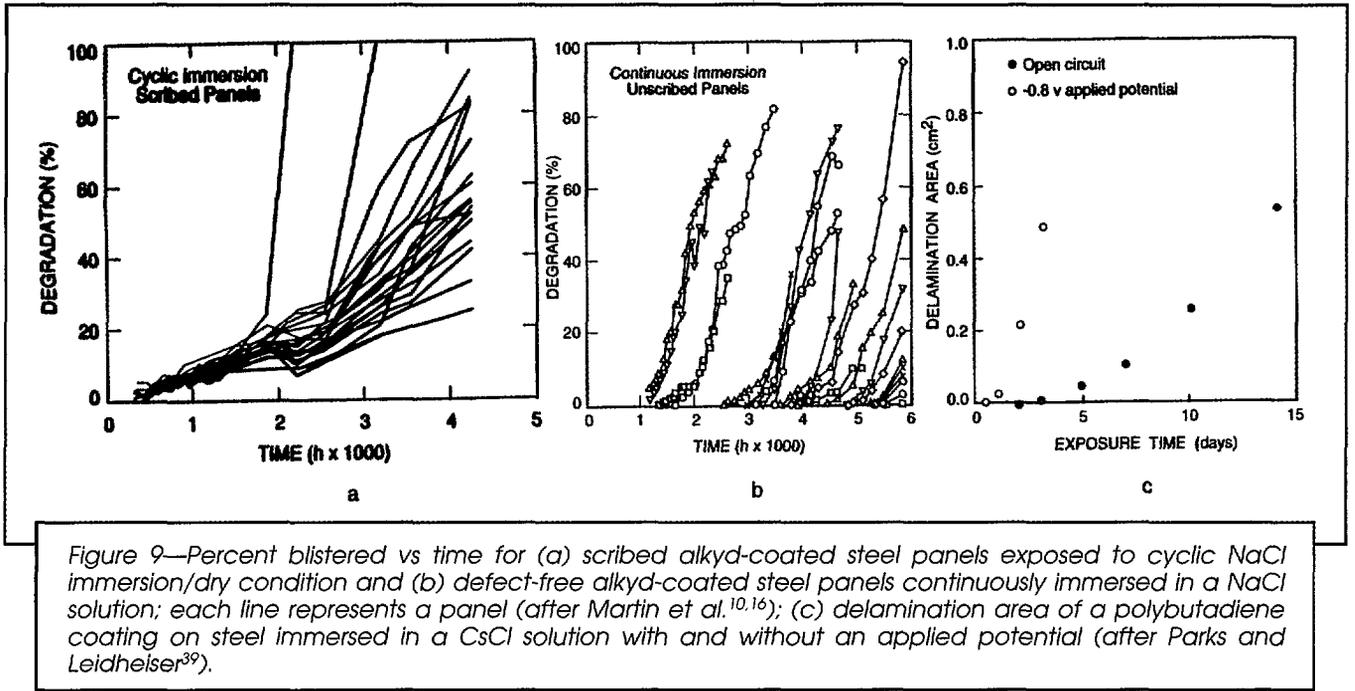


Figure 9—Percent blistered vs time for (a) scribed alkyd-coated steel panels exposed to cyclic NaCl immersion/dry condition and (b) defect-free alkyd-coated steel panels continuously immersed in a NaCl solution; each line represents a panel (after Martin et al.^{10,16}); (c) delamination area of a polybutadiene coating on steel immersed in a CsCl solution with and without an applied potential (after Parks and Leidheiser³⁹).

where $C = C'/C_0$, $t = Dt'/L^2$, $L = R - a$, and $r = r'/(R - a)$, C_0 is the cation concentration in the environment; R is the distance between the defect and blister; and a is the radius of the blister. There are two dimensionless parameters in this model: the geometric aspect ratio, $k=a/R$, and the potential gradient parameter, $p = \mu(\Delta\phi)/D\log(l/k)$; $\Delta\phi$ is the potential difference between the defect and the blister.

Nguyen, Hubbard, and McFadden⁷³ solved the previous set of equations numerically and presented graphical results of the dimensionless concentration profiles and flux as functions of these parameters. Pommersheim et al.⁷⁵ have provided the analytical solutions of these equations for the steady-state. The models predict that, after a delay, the flux into the blister, and hence the cathodic blistering, increases rapidly with exposure time. The flux increases as the blister size increases or the distance between the blister and the defect is reduced. For two blisters of the same size and under the same potential gradient between the defect and blister, a blister that is one-fifth of the distance from the defect will have almost twice the amount of cation flowing into it. The models also imply that cation flux should increase almost linearly with applied potential between the defect and the cathodic blister. This prediction is in good agreement with Stratmann's results for a variety of coatings, which showed that the rate of cathodic delamination increased linearly with the potential difference between the defect and any location at the coating/metal interface.⁷² Based on these models, as long as the adhesion of a coating around a defect is maintained so as to minimize cation migration from the defect area to the potentially blistering area, the cathodic blistering around a defect will be minimized.

We refined these models further by proposing that the transport of cations to the blister-initiating sites takes place in two stages: an initial induction and a subsequent propagation period.^{75,76} In the induction period, cations diffuse and are adsorbed on the walls of the "interfacial gap" between the coating and the metal substrate. The problem is the diffusion of a boundary interface, which is described by equations (7)

and (8) for the presence and absence, respectively, of a radial potential gradient.

$$\frac{dr_i}{dt} = \frac{D \delta C_0 p}{\bar{p}_s r_i} \frac{1}{\left(\frac{r_i}{R}\right)^p - 1} \quad (7)$$

$$\frac{dr_i}{dt} = \frac{D \delta C_0}{\bar{p}_s r_i} \frac{1}{\ln \frac{r_i}{R}} \quad (8)$$

where \bar{p}_s is the amount of adsorbed cation per unit of interfacial area, r_i is the distance between the moving boundary (cation adsorbed site) and the center of the blister, and δ is the (average) thickness of the interfacial gap between the coating and the metal. These equations predict the rate at which cations move from the defect towards the cathodic blister. Solutions for the equations expressing the times required for cations to reach the blister were also derived.

The propagation period occurs after the cations have reached the cathodic blister sites. In this stage, cations enter the blister as a result of both diffusion and facilitated transport caused by the potential differential between the cathodic sites and the defect. The concentration of cations moving into the blister may be expressed by the following equation:

$$\frac{dC_A}{dt} = \frac{2\pi \delta D}{V \ln(1/k)} \left[C_0 - C_A \left(1 - \frac{k \ln(1/k)}{1-k} p \right) \right] \quad (9)$$

where V is the volume of the solution in the blister. Integrating provides an expression for the concentration of cations within the blister as a function of time.

$$\frac{C_A}{C_0} = \frac{1}{a} \left[1 - e^{-a\beta(t-\theta_i)} \right] \quad (10)$$

where $a = 1 - \frac{k \ln(1/k)}{1-k}$, $p = 1 - \left(\frac{p}{p^*}\right)$, $\beta = \frac{2\pi \delta D}{V \ln(1/k)}$

Θ_i is the induction time, Θ_i can be determined from the solution of equation (6) by the time where cations first arrive at the blister ($r_i=a$). p^* , which is equal to $(1-k)/k \ln(1/k)$, is defined as the critical value of the potential gradient and depends on the size of the blister and the separation between the anodic and cathodic regions.

An experiment on the diffusion of cations along the coating/metal interface was carried out to verify the predictions of equation (10) in the presence of a potential gradient between a defect and a blister.^{76,82} The experiment measured the concentration of sodium ions *in situ* (using a sodium selective microelectrode) in an artificial, simulated cathodic "blister." Figure 8 schematically presents details of the experiment. The sodium ion migrated along the coating/metal interface from the defect (in contact with a 0.5 mol/L NaCl solution) to the blister (containing distilled water initially) under an applied potential of $-0.85V$ (vs. an Ag/AgCl reference electrode) between the defect and the blister. The pH in the blister was continuously monitored and was in the range between 10.2 and 11.0 after an induction period of about 335 hr. The metal in the blister remained uncorroded during more than 800 hr of measurements. The whiteness of the metal and the high pH in the blister indicated that the experiment was successful in simulating the cathodic blistering of organic-coated steel. Complete experimental details and results are given elsewhere.⁷⁶

Figure 8 displays both theoretical equation (10) and experimental data of sodium ion concentration versus time within the blister for an induction time Θ_i of 288 hr. Sodium ions have not broken through into the blister for times less than Θ_i . The induction period is shown as a horizontal line along the axis of Figure 8. The results over the full time range show good agreement between experimental data and theoretical predictions. The upward trend of the data is in accord with the theory. Equation (10) predicts that the blister will keep enlarging as long as there are sufficient sodium ions in the external solution and the potential gradient is equal to or greater than the critical value ($p \geq p^*$). The theory also predicts that small blisters will not grow until or unless a critical potential value (p^*) is reached. Blisters of larger size can grow under the combined effects of cation transport, osmosis, electro-osmosis, cathodic delamination, and mechanical stress. The shapes of the curves in Figure 8 (both induction and propagation periods) are in agreement with the experimental results on cathodic blistering obtained by Martin et al.^{10,16} for scribed and unscribed alkyd-coated panels continuously immersed in a 0.8 mol/L NaCl solution or exposed to cyclic NaCl immersion/dry condition (e.g., Figures 9a and b). The predictions were in agreement with cathodic delamination results of Parks and Leidheiser³⁹ for polybutadiene coatings on steel panels immersed in a 0.50 mol/L CsCl solution, both with and without a $-0.8V$ applied potential (e.g., Figure 9c), and of Stratmann et al.^{7,72} for a variety of coatings on surface-pretreated and untreated steel panels exposed to NaCl electrolytes.

SUMMARY AND CONCLUSIONS

A unified model, consisting of both conceptual and mathematical components, has been developed to describe various steps in the degradation of organic protective coatings on a steel panel exposed to a neutral electrolyte. The model for the

initiation of degradation of coatings containing no apparent defects (good or multilayer coatings) was based on the concept that ions reach the substrate surface by transport through conductive pathways in the coatings. Pathway formation is due to water attack in the hydrophilic, low-molecular-weight/low-crosslinked regions in the coatings, followed by interconnections of these regions. The models for cathodic blistering resulting from corrosion reactions are based on the transport of the alkali metal ions along the coating/steel interface from the conductive pathways or defects to the blisters. Theoretical predictions agree well with results of a cation diffusion experiment, which was carried out in the presence of a potential gradient. The predictions are also in agreement with experimental results on the cathodic blistering and delamination of coated panels exposed to electrolytes. The development of quantitative, physical models to describe the degradation of coated metals should greatly enhance our ability to develop effective protective coatings for metals.

ACKNOWLEDGMENTS

We wish to thank Dr. J. Martin, Building and Fire Research Laboratory, NIST, for providing the photographs in Figures 1a and 1b.

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Addendum

During review, we came across two recent studies providing further evidences to support the conceptual model proposed in this paper. The first article was from an investigation by Tan et al.⁸³ who used an array of 121 isolated microelectrodes to probe at the inhomogeneity in films made with phenolic, alkyd, and polyurethane coatings. They showed that these coatings possessed regions of low D.C. resistance (D type) and that the area of these regions increased with increased time of exposure to three percent NaCl solution. These results further support our suggestion that organic films contain water-susceptible, hydrophilic regions where conductive pathways develop and enlarge during exposure. The second study was by Miskovic-Stankovic et al.⁸⁴ who investigated the penetration of NaCl solution in the microstructure of an isocyanate-modified epoxy coating electrodeposited on a steel substrate. Based on results obtained by A.C. impedance spectroscopy, water and electrolyte uptake, and optical microscopy/image analysis, they concluded that the degradation of the coating consisted of two steps: water uptake followed by water and ions penetration through the macropores. This conclusion is consistent with our view on the initial step in the degradation of a good or multilayer coating that water degrades and opens conductive pathways in the hydrophilic regions of the films, allowing ions to reach the metal surface.