

* Fourth Place Winner 1998 Roon Awards Competition *

Micro-Mechanic Model for Cathodic Blister Growth in Painted Steel

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INTRODUCTION

The use of polymer coatings is the most common and economical means to protect metals against corrosion. Despite great advances in coatings technology in recent years, coatings eventually lose their protective properties whereupon corrosion of metals will occur under the coating. One of the most severe degradation modes is the so-called “cathodic blistering” (due to the cathodic half-cell reaction of the corrosion process), which occurs when certain coated steel panels are exposed to a salt environment. This phenomenon is often observed on polymer-coated steel panels with or without apparent damages in the coatings, e.g., a dented car fender or a bridge beam. If the effectiveness of protective coatings is to be increased, it is essential to develop physics-based models for quantifying the growth of cathodic blistering. This paper presents a micro-mechanic model to predict the growth rate of cathodic blisters when a coated steel panel is exposed to a neutral or an alkaline solution containing salts.

Cathodic blister initiation is always associated with some form of defect in the coatings, such as artificial scribed mark¹⁻⁴ (see Figure 1a) small pores,² or conductive pathways developed during exposure⁵ (see Figure 1b). Defects and pathways through coatings provide direct channels for the transport of ions from the environment to the steel surface where corrosion processes occur on the steel surface at and around the defects. In a neutral salt solution, the anodic reactions take place at the defects^{2,6,7}; however, in an alkaline environment, anodic reaction products have been observed to form under the coating and away from the defects.⁸ In either neutral and alkaline salts, cathodic reactions take place under the coatings in the vicinity of the corroded areas (the anodes), and the products generated by the cathodic reactions have been proposed as the cause of the disbondment (hence the term cathodic disbondment or delamination) of the coatings from the substrates.^{1,2,9}

The disbonded areas under the coatings where cathodic reactions occur serve as the blister nucleation sites. Detail of the cathodic blister initiation sites and

A micro-mechanic blister growth model is proposed for a coating system consisting of a polymer film applied to a steel substrate exposed to salt solutions. The mechanism of the blister formation is based on corrosion-induced disbondment of the coating at the defect periphery coupled with the stress driven diffusive transport of liquid along the coating/substrate interface. By considering the coating as a semi-double cantilever beam loaded by a moment at the periphery and a distributed load along the beam length due to mass transport, a fifth order ordinary differential equation is derived for the beam deflection. The solution is obtained, which yields the functional relationship between the blister growth rate and applied bending moment. The predicted blister growth velocity compared favorably with experimental observations on a paint coated steel panel immersed in a five percent salt water solution. Model predictions allow the construction of a blistering zone/non-blistering zone map, which should help to design better protective coatings for steel.

their location is probably a stochastic process. They may be initiated from imperfections in the coating/steel (oxide) bonds, micro voids at the coating/steel interface, or “defect” areas on the steel surface. Regardless of the location, an incubation time is always required for the initiation of a cathodic blister on polymer-coated steel

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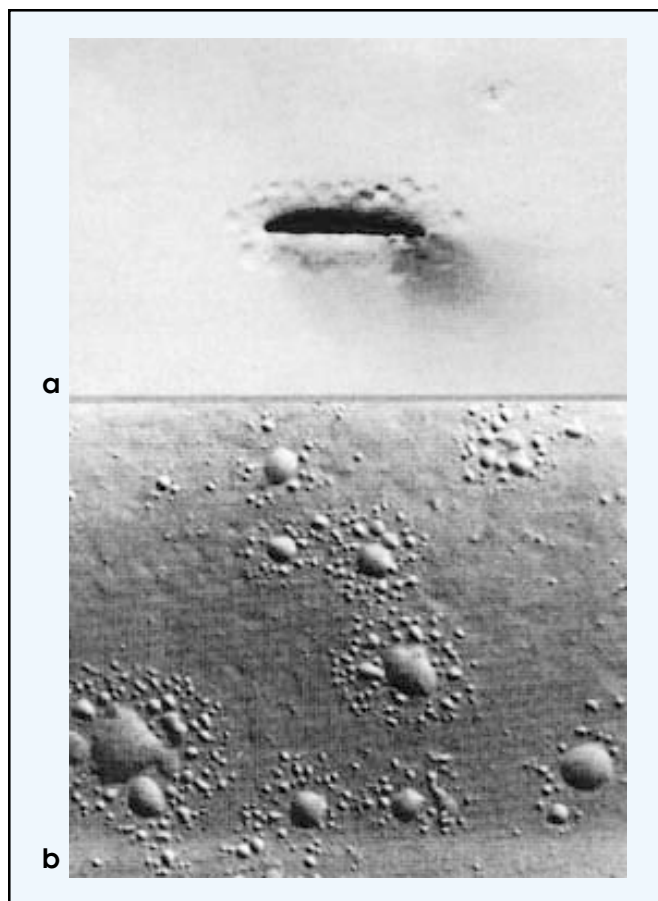


Figure 1—Photographs of cathodic blistering of painted steel in a neutral electrolyte: (a) with a large defect, and (b) without initial defects.

panels. For panels containing no apparent defects or small pores, the time it takes for cathodic blisters to occur is much longer than for panels containing defects.^{3,10}

The issue of cathodic blister growth is a subject of debate. There are generally two schools of thought with regards to the driving force. Funke² believed that osmotic pressure is the main mechanism responsible for the growth of a cathodic blister. However, for some coatings, Martin et al.¹⁰ have proposed that, after the blister is formed, a bending moment is set up at the periphery or “tip” of the blister to drive diffusive flux of the cathodic reaction products, leading to the enlargement of the blister. In this case, since the driving force is not from the liquid pressure buildup inside the blister cavity (it is from the bending moment present inside the coating), it is called non-osmotic blistering process. Regardless of which school of thought, the driving force always comes from a bending moment derived either from the pressurized liquid present inside the cavity of the blister nuclei or from the residual compressive stresses present in the polymer coating that has been immersed in the salt solution. Dickie¹¹ has discussed the role of mechanical stress on coatings failure and believed that the applied stress can change both the rate and the mecha-

nism of corrosion process. He further indicated that the role of stress in the corrosion-induced adhesion loss is not well understood and recommended a careful study on the interaction of chemical and physical processes under controlled conditions to evaluate the durability of protective coating systems.

This paper adopts the concept of the nucleation idea wherein it is assumed that a blister is initiated at a cathodic site and reaches a critical nuclei size. It then starts to grow in a steady-state manner at an unknown (a priori) constant velocity driven by the applied bending moment at the periphery. Under the action of an applied bending moment (produced either by osmotic or non-osmotic process), the liquid in the cathodic blister is driven laterally along the coating/substrate interface to the cathodic disbondment front, causing the coating to deform. The Fick’s diffusion law links this deflection field with the distributed loads along the beam length. By considering the coating as a semi-double cantilever beam (double-cantilever beam specimens are well known in the mechanics community for testing fracture properties), a differential equation for the unknown deflection can be derived based on the principle of strength of materials. Details are presented in the following section. The end result is an equation to predict the steady-state blister growth rate as a function of the applied bending moment, film thickness, and elastic properties of the coatings, diffusive characteristics of ions along the coating/substrate interface, and exposure temperature. In the Discussion Section, we test the applicability of the present theory using experimental data given by Martin et al.¹⁰ in which blister growth rates were measured for an alkyd primer/topcoat system applied to a sandblasted steel substrate immersed in a neutral 5 mass% of NaCl solution at 30°C. The good agreement between the theory and experimental data suggests that the model can potentially be used for predicting the growth rate of cathodic blisters, and, ultimately, the service life of a coating system. Further, the model can assist the engineer to design better protective coatings against the corrosion of steel.

MODEL FOR BLISTER INITIATION AND GROWTH

Blister Initiation

During the curing process, the volume of a polymer coating/steel system decreases introducing an in-plane residual tensile stress in the coating. When the coated panel is immersed in a water solution containing salt, water gradually diffuses into the coating film leading to swelling with a volume expansion of the film. The swelling-induced in-plane stress has been reported so high that the residual stress state of an epoxy can change from 10 MPa in tension to 5 MPa in compression.¹² Martin et al.¹⁰ briefly reviewed the cause of buckling due to hygroscopic stresses for polymer coatings. For coated steel panels exposed to electrolytes, an electrochemical cell is established when corrosive species, i.e., water, oxygen, and ions, reach the steel surface where iron is consumed

at the anodes and oxygen is reduced at the cathodes. As mentioned earlier, the cathodic-induced disbonded areas serve as the blister nucleation sites. When the size of these areas reaches a critical value, buckling of the coating due to the compressive stress or the pressurized liquid in the cavity occurs. This will result in the formation and enlargement of cathodic blisters.

If we let w be the buckling distance or the height of the non-osmotic blister, then a bending moment M_o per unit length of the blister circumference (expressed in $N \cdot m/m$) due to the residual compressive stress σ_r will be introduced at the "tip" of the blister

$$M_o = \sigma_r h w \tag{1}$$

where h is the total coating thickness (including topcoat and primer). In addition, there is a horizontal concentrated force $F = \sigma_r h$ per unit width developed at the tip; this force will generate extra bending moment on the blister. However, because w is $\gg h$, this extra moment is secondary so long as the coating undergoes only a small deformation, and thus will not be considered hereafter.

For the case of osmotic cathodic blistering, the bending moment per unit width of the blister circumference can be expressed as a function of the pressure of the liquid in the blister cavity, p , and the radius of the blister nuclei, r , as given by¹³:

$$M_o = \frac{1}{8} p \cdot r^2 \tag{2}$$

If we let σ_f be the cathodic disbondment stress, then the interfacial stress σ_o at the blister tip (where the cathodic disbonded area and non-cathodic disbonded area is separated) must always be the disbondment stress σ_f , namely,

$$\sigma_o = \sigma_{yy}(0) = \sigma_f \tag{3}$$

Here, σ_f is defined as the tensile stress of the coating/substrate system (i.e., the interfacial tensile strength) below which the coating does not disbond from the substrate; the subscript o denotes the location of the blister tip, namely $\sigma_o = \sigma(0)$.

Blister Growth

Once the blister has been formed, it can grow at a steady-state velocity V under the action of the applied bending moment M_o located at the periphery of the blister. This study aims to derive a physics-based model to compute V as a function of M_o , material stiffness (in exposure condition), coating/steel bonding strength while immersion in solution, coating thickness, and exposure temperature. Therefore, the model should be able to predict the service life of a coating system exposed to electrolytes at a given temperature. In order to achieve this goal, a mathematical model is formulated in which Fick's laws and the principle of strength of materials are injected to form a well-defined boundary value

problem. Those tasks are described in the following subsections.

LIQUID TRANSPORT AT THE COATING/METAL INTERFACE: Consider mass transport of liquid (electrolyte in this case) along the coating/steel interface at the cathodic blister tip (see schematic sketch of the model in Figure 2). When the radius of the blister is large enough compared with the blister height, plane-strain conditions in steady-state prevail because the radius of curvature of the periphery in the x - z plane (here the z -axis is perpendicular to the plane of the paper) is large in comparison with that of the tip radius in the x - y plane. Accordingly, the problem can be treated as two dimensional on a unit thickness basis in the z -direction. The biaxial stress state in the coating film can be handled via the effective stiffness. We can then consider the tip as a straight tip front along the z -axis moving at a velocity V in the x direction in a moving Cartesian coordinate x - y system with its origin attached to the propagating blister tip.

The chemical potential at any location along the coating/substrate interface can be expressed as $\mu(x) = -\Omega \sigma(x)$ where Ω is the volume of the diffusing species and $\sigma(x) = \sigma_{yy}(x)$ is the normal stresses at location x along the interface. Fick's law then dictates that the diffusive flux be in inverse proportion to the gradient of the chemical potentials. Thus,

$$J(x) = -\frac{D_b \delta_b}{kT\Omega} \nabla \mu(x) = \frac{D_b \delta_b}{kT} \frac{d\sigma}{dx} \tag{4}$$

where J is the matter flux at the interface, D_b is the interfacial diffusion coefficient of the liquid, δ_b is the thickness (gap between the coating and the substrate) of the diffusion channel, and kT has its usual meaning. At the steady-state, the blister volume grows at $(w \cdot V)$ per unit length per unit time. Matter conservation then requires that the matter flux at the tip $J(0) = J_o = wV/\Omega$. This combination with equation (3) then gives

$$\sigma_o' = \frac{w kT V}{D_b \delta_b \Omega} \tag{5}$$

where $\sigma' = d\sigma/dx$ is the first derivative of stress with respect to x , and subscript o denotes tip location at $x = 0$.

A SEMI-DOUBLE CANTILEVER BEAM MODEL: From the perspective of the mechanics, the interface between the

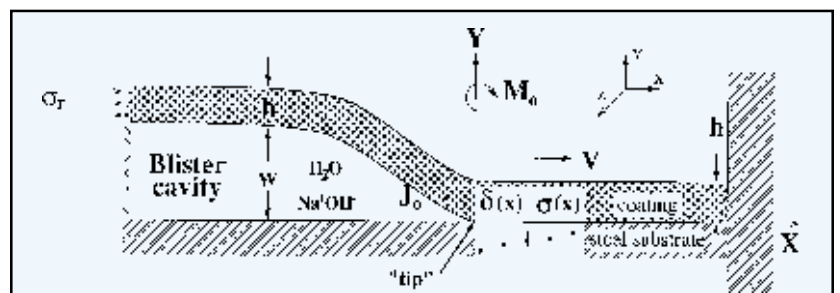


Figure 2—Schematic of the proposed cathodic blister growth model. The coating is modeled as the cantilever beam lies on an elastic foundation loaded by a moment at one end.

(9)

coating and the substrate can be modeled as a series of springs (whose strength represents the local interfacial bonding strength) connected between the two entities (i.e., the coating and the substrate), as envisioned by Martin, et al.¹⁰ (see Figure 6 in reference (10)). However, due to electrolyte diffusion along the interface, as discussed in the previous subsection, the springs will be deformed to certain amounts dictated by Fick's laws. Accompanying with the deformation, the springs will also exert forces in proportion to the spring displacements on the coating as well as on the substrate. If we take a free body of the coating, as presented schematically in Figure 2, it can be modeled as one-half of a double cantilever beam located along the positive x-axis with a unit thickness in the z-direction rested on an elastic foundation. Note that double-cantilever beam specimens are popular in the fracture mechanics community for measuring the toughness of the material under consideration. The blister cavity is located at $x \leq 0$, and the tip at $x = 0$ is moving at a constant speed V in the positive x-direction. In addition to the distributed loads imposed by the springs, the beam (i.e., the coating) is subjected to a bending moment M_0 applied at the tip $x = 0$ due to the residual compressive stresses as computed by equation (1) or liquid pressure inside the blister cavity, as given by equation (2). If we express local deflection of the film as $\delta(x)$ and local externally applied stress from the spring foundation to the coating as $\sigma(x)$, then the principle of the beam on elastic foundation in the discipline of the strength of materials demands that they must be related by the following equation for the beam:

$$\frac{Eh^3}{12(1-\nu^2)} \frac{d^4\delta}{dx^4} + \sigma(x) = 0 \quad (6)$$

for $x \geq 0$. Here E is the effective Young's modulus of the coating obtained in the wet (exposure condition) ν state, ν is the Poisson's ratio of the coating, and h is the total coating thickness including the topcoat and primer. Since the coating is in a biaxial stress state, the effective stiffness E is equal to the true Young's modulus divided by $(1-\nu)$.

Meanwhile, at an arbitrary location x , under steady-state conditions the local deflection, $\delta(x)$, must be related to the flux as $\delta(x) = \Omega \cdot J(x) / V$, due to mass conservation requirement. After combining with equation (4), $\delta(x)$ becomes

$$\delta(x) = \frac{D_b \delta_b \Omega}{kT V} \frac{d\sigma}{dx} \quad (7)$$

Upon substituting equation (7) into equation (6) to eliminate the stress variable, we finally arrive at a fifth order ordinary differential equation for the unknown local deflection $\delta(x)$ of the beam:

$$L^5 \frac{d^5\delta}{dx^5} + \delta = 0 \quad (8)$$

where L has a unit in length, and can be expressed by

$$L = \left[\frac{Eh^3 D_b \delta_b \Omega}{12(1-\nu^2)kT} \right]^{1/5} \quad (9)$$

The boundary conditions at the blister tip are as follows:

$$-\frac{Eh^3}{12(1-\nu^2)} \delta_0^{(IV)} = \sigma_0 \quad (10)$$

according to equation (3), and, furthermore,

$$-\frac{Eh^3}{12(1-\nu^2)} \delta_0^{(V)} = \sigma_0' \quad (11)$$

according to equation (5). Here the superscripts (IV) and (V) denote fourth and fifth derivatives, respectively. Moreover, the shear stress at the tip must vanish. This means that

$$\delta_0^{(III)} = 0 \quad (12)$$

In addition, it is assumed, based on physical arguments, that both $\delta(x)$ and $\delta'(x) \rightarrow 0$ as $x \rightarrow \infty$. The differential equation (8) together with the boundary conditions (equations (10-12)) forms a well-defined boundary value problem so that a unique solution is guaranteed. This mathematical problem has been solved by Chuang,¹⁴ and the solutions can be expressed as a function of three functions superimposed together: exponential, exponential times sine, and exponential times cosine functions. Plots of the tensile stress as a function of distance from the blister tip along the coating/substrate interface indicate that both the stresses and deflections are cyclically varied with decaying amplitudes. Since the bending moment is proportional to the second order derivative of the deflection with respect to x , we are finally able to express M_0 at the tip as¹⁴

$$M_0 = L^3 \sigma_0' + \frac{1+\sqrt{5}}{2} L^2 \sigma_0 \approx L^3 \sigma_0' + 1.62 L^2 \sigma_0 \quad (13)$$

Substituting the expressions for L from equation (9), σ_0' in equation (5) and σ_0 in equation (3) into equation (13), we obtain the relationship between the applied moment at the tip and the steady-state blister growth rate:

$$M_0 = A \cdot V^{2/5} + B \cdot V^{-2/5} \quad (14)$$

where A and B can be expressed as follows in terms of the coating's material properties and exposure temperature:

$$A = \frac{w}{\Omega^{2/5}} \left[\frac{kT}{D_b \delta_b} \right]^{2/5} \left[\frac{Eh^3}{12(1-\nu^2)} \right]^{3/5} \quad (15)$$

$$B = 1.62 \cdot \sigma_i \left[\frac{Eh^3 D_b \delta_b \Omega}{12(1-\nu^2)kT} \right]^{2/5} \quad (16)$$

A close examination of equation (14) indicates that there is a threshold bending moment $(M_0)_{th}$ below which the blister will cease to grow:

$$(M_0)_{th} = 2\sqrt{AB} = 0.73 \sqrt{\frac{Ew\sigma_i h^3}{1-\nu^2}} \quad (17)$$

At this loading level, a minimum blister growth rate is predicted:

$$V_{\min} = \left(\frac{B}{A}\right)^{\frac{5}{4}} = 1.83 \cdot \left(\frac{\sigma_r}{w}\right)^{\frac{5}{4}} \left[\frac{D_b \delta_b \Omega}{kT}\right] \left[\frac{E h^3}{12(1-\nu^2)}\right]^{-\frac{1}{4}} \quad (18)$$

below which the blister cannot propagate at all. This feature of non-vanishing velocity has the origin from thermodynamics and will be discussed in more details later. Equation (14) can be written in a non-dimensional form in terms of the normalized moment, m , and the blister growth velocity, v :

$$v = \left[m + \sqrt{m^2 - 1}\right]^{\frac{5}{2}} \quad (19)$$

for $v \geq 1$ and $m \geq 1$. Here, $v = V/V_{\min}$ and $m = M_o/(M_o)_{th}$ are the normalized velocity and normalized moment, respectively. Figure 3 plots the predicted blister growth velocity as a function of bending moment applied at the tip. When $m \gg 1$, it is seen from the figure and equation (19) that the blister growth rate is predicted to increase with increasing m to the power of 2.5. It should be noted that Martin et al.¹⁰ have estimated a critical moment for blister initiation, which, using our notation, takes the following form:

$$M_{ini} = 3 \frac{Eh^3w}{a^2} \quad (20)$$

where $a = 2r$ is the diameter of the blister nuclei at the initiation. It is noted that the Euler equation,¹³ which was used as equation (5) in reference 10 to calculate the coating's buckling load, is given as $P_c = 4EI\pi^2/l_u^2$. This expression has the same form as equation (20) if we realize $P_c = M_{ini}/w$, $l_u = a$, and $I = h^3/12$. In the previous expression, P_c is the critical load at which the coating buckles, l_u is the diameter of the disbanded area, and I is the moment of inertia of the coating. It is interesting to compare the bending moment levels of equations (17) and (20). For instance, if the bending moment predicted by equation (17) is less than that predicted by equation (20), then the blister will not grow even if it is initiated. On the other hand, if the value calculated by equation (17) is larger than that predicted by equation (20), the blister may grow after its formation.

It is worthwhile to compare the current blister growth model with the blister adhesion test method, which was first proposed by Dannenburg¹⁵ and later analyzed and developed by Williams.¹⁶ This test has been used to measure the adhesive fracture energy of various polymer film/substrate systems.¹⁷ In a typical blister adhesion test, a coating is bonded to a rigid adherend except for a central region of radius r . A compressed fluid such as air or liquid is injected into the unbonded region to lift the coating, thereby forming a blister whose radius is fixed such that the whole system is in equilibrium. Increasing the fluid pressure will increase the blister size until the critical pressure is reached. At the critical pressure p , the blister increases unstably, indicating failure of adhesion. The principle of this test is derived from the theory of linear elastic fracture mechanics where the

concept of stress intensity factor K and its relationship to the elastic energy release rate or fracture energy $G_a = K^2(1-\nu^2)/2E$ are established.¹⁸ We further note that in the case of double-cantilever beam specimens, K is related to bending moment at the tip by^{14,18}

$$K = M_o \sqrt{\frac{12}{h^3}} \quad (21)$$

Substituting equation (2) into equation (21) to eliminate M_o and using the G_a - K relationship to eliminate K , we obtain the equation (22) for expressing G_a in terms of the critical pressure p , the coating thickness h , the blister radius r , and the elastic properties of the coatings E and ν :

$$G_a = \frac{3r}{32} \frac{1-\nu^2}{E} \left(\frac{r}{h}\right)^3 p^2 \quad (22)$$

which has the same form as the equation used for the blister adhesion test.¹⁶

In mechanics terms, the current model is essentially the same as the blister adhesion test, except that the mass transport driven by the bending moment at the blister tip (treated in this study) is allowed to occur at the coating/adherend interface. In the context of thermodynamics, the current model is in compliance with non-equilibrium or irreversible thermodynamics where diffusive flux generates heat for entropy production. The blister adhesion test is consistent with equilibrium thermodynamics where the process is fully reversible.

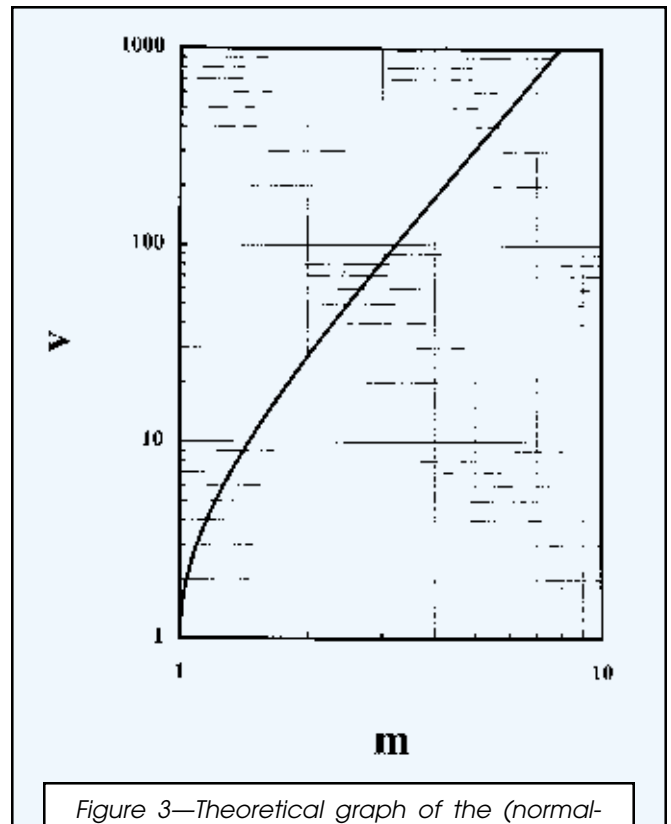


Figure 3—Theoretical graph of the (normalized) cathodic blistering velocity, v , as a function of (normalized) moment, m , in a log-log scale.

Table 1—Values of Parameters Used for Model Verification

ν	$h(\mu\text{m})$	$w(\text{mm})$	$\sigma_f(\text{MPa})$	$D_b\delta_b(\text{m}^3\text{s}^{-1})$	$\Omega(\text{m}^3)$	$T(\text{K})$
0.4	145.0	3.0	-5.0	2×10^{-13}	1×10^{-29}	300

COMPARISON WITH EXPERIMENTAL RESULTS

To test the validity of the proposed blister growth model, data collected from the experiment performed by Martin et al.¹⁰ were used for the prediction. In order to determine the applied moment M_0 and the blister growth rate V , data of E , $D_b\delta_b$, σ_f , σ_r , h , Ω and ν must be known. The values of these parameters, which are given in Tables 1 and 2, are obtained from the following sources: h (coating thickness), w (blister height), and σ_f (the residual compressive stress) given in Martin et al.,¹⁰ ν (Poisson's ratio of the coating) and E (Young modulus of an alkyd coating) at 30°C taken from data of Perera and Eynde,¹⁹ Ω (volume of the diffusing species) given in reference (20) over a wide range of species with $1.0 \times 10^{-29} \text{ m}^3$ as a typical value.

The diffusion coefficient-disbondment thickness product, $D_b\delta_b$, is taken from the result of Pommersheim et al.,²¹ which was calculated from a diffusion model using data of an experiment of Na^+ ion (from 3.5 mass% of NaCl in water) transport along the coating/steel interface from a defect. The use of this data for the verification of the blister growth model is valid because, as corroborated later in the discussion, Na^+ ions transport along the coating/steel interface from the defects to the cathodic sites is the main process responsible for the formation of the highly alkaline NaOH solution at the disbondment front. Thus, this transport process can be used to characterize the diffusion of electrolyte from the interior to the cathodic blister tip.

The value of σ_f , the tensile stress below which the coating does not cathodically disbond from the substrate, is obtained based on results from two experimental data sets. The first set of data is from a study by Walker,²² who used the pull-off test to observe that alkyd coatings on stainless steel immersed in condensed water at 45°C lost their adhesion rapidly within 50 hr, but remained constant thereafter. The second set of data is from the results of Nguyen and co-workers,^{8,23} who employed a wet peel adhesion test to show a sharp, distinct separation between the cathodic-disbonded and the water-induced adhesion loss regions of epoxy-coated steel panels immersed in an alkaline solution containing a mass fraction of 3.5% NaCl. They also observed that the water-induced adhesion loss reached a minimum value and recovered most of its strength after drying⁸; the minimum observation is consistent with Walker's results. On the other hand, the cathodic-disbonded region completely lost its bonding strength, which did not regain any of it after drying. Further, they found no evidence of a transition between the water-induced adhesion loss and cathodic-disbonded regions. That is, as the specimen was peeled from the

water-induced adhesion loss zone to the cathodic-disbonded zone, the peel strength dropped vertically from a certain value to zero. Based on this evidence, the

minimum value of the water-induced adhesion loss is chosen as σ_f for the calculation. That value for an alkyd coating on a stainless steel exposed to water, which was recorded by Walker,²² is given in Table 1. This selection also implies that, σ_f at $x = 0$ coincides with the cathodic-disbondment front.

Table 2 presents the calculated applied bending moment at the blister tip using equation (1), the predicted blister growth velocity as given by equation (19), and the observed velocity given by Martin et al.¹⁰ for a given value of E and σ_f . It is evident from this table that the velocity predicted by the current theory is in good agreement with the experimental observation. In addition, the calculated threshold applied moment, M_{th} is 2.01 N·m/m, which is about 92% of the applied bending moment, and the minimum steady-state blister growth velocity is 0.55 nm/s, which is about 0.37 times lower than the predicted blister growth rate. Now, the blister nuclei size, a , should be in the same order of magnitude of w , the blister height. If we assume $a = 5 \text{ mm}$, then the initiation moment required as computed from equation (20) is 0.55 N·m/m, which is less than the threshold level for growth. This means that once the blister is formed, the model predicts that the blister may or may not start to grow after initiation, depending on the level of the applied moment.

The use of data from different sources experimented under different conditions for model validation deserves some comments. As indicated earlier, we used experimental results of Martin et al.¹⁰ for blister growth of an alkyd topcoat/primer system applied to a steel panel immersed in a 5 mass% NaCl solution at 30°C for the verification. However, reference (10) does not provide data on E , σ_f , and $D_b\delta_b$ needed for the calculation. Of course, it would be more desirable to have the blistering results and material parameter data from the same coating system exposed to the same environment. However, we believe that even such an ideal situation will have little impact on the verification and validity of the model. The reason for that is, even for the same experimental conditions, the value of σ_f , $D_b\delta_b$, and E are, at best, an approximation. As indicated earlier, both σ_f and $D_b\delta_b$ are parameters that are very difficult to measure accurately. For example, σ_f was taken as the minimum of the water-induced adhesion loss data based on the observation that there is no transition zone between the water-induced adhesion loss and the cathodic disbondment. Does this adhesion loss minimum truly represent the critical interfacial strength below which the coating does not cathodically disbond from the substrate? or is there

Table 2—Applied Bending Moment and Predicted and Observed Blister Growth Velocities at a Given Value of E and σ_f

$E(\text{GPa})$	$\sigma_f(\text{MPa})$	$M_0(\text{N}\cdot\text{m}/\text{m})$	$V_{\text{predict}}(\text{nm}/\text{s})$	$V_{\text{measured}}(\text{nm}/\text{s})$
0.5	1.4	2.18	1.47	1.86

another value somewhere between the water adhesion loss minimum and the value that causes the cathodic disbondment? Similarly, there are a number of uncertainties about the value of $D_b\delta_b$ parameter for a practical polymer coating/metallic substrate system exposed to a corrosive environment. For such a complex system subjected to not-well control experimental conditions, $D_b\delta_b$ may be best estimated from calculation, as described in reference (21), because there is no method in existence to measure δ_b of a polymer/steel interface. Other interesting questions on δ_b are: does its value vary with blister size, type of coatings, or type of electrolyte, etc?

The effect of moisture and exposure temperature on E value is also complex. This is because not only E of a polymer may decrease due to water plasticization but also is drastically reduced above its glass transition temperature (T_g). The latter effect can occur in coatings whose T_g at use conditions is close to the temperature of exposure. Even for the plasticization, the effect is different for different polymers. For example, DeNe and Shahanan²⁴ reported a reduction in E of an amide-cured epoxy ($T_g > 50^\circ\text{C}$) after aging in 100% RH for 1000 hr, but Perera and Eynde¹⁹ observed little change in E of an amine-cured epoxy (dry $T_g = 98^\circ\text{C}$) between dry and 90% RH. The latter authors also showed that E of the two alkyds that have dry T_g values close to room temperature (28 and 32°C) decrease substantially with increasing humidity. In summary, because of measurement uncertainties of material parameters involved in a practical polymer coating/metal system subjected to a corrosive environment, even under the best experimental conditions, the use of values from different sources should not affect the validity of the current model. That is, giving adequate material properties, the model developed in this study can give a good prediction of the growth rate of cathodic blisters of coated steel exposed in electrolytes. On the other hand, by knowing the blistering rate, the model can provide an estimate of the disbondment stress or the coating modulus that would prevent cathodic blistering of coated metals.

DISCUSSION

A basic assumption of the current blister growth theory is that steady-state conditions prevail. This is supported by the experiment performed by Martin et al.¹⁰ who observed that after a short period of transient state, the blister grows in a steady-state fashion at a fairly constant velocity for a prolonged period. The physical requirements for maintaining a steady-state are that the driving force (i.e., the moment at the tip in this case) as well as other field parameters must remain invariant with respect to the moving coordinate system. To keep the moment constant at the moving blister tip with increasing blister radius r , either one of the following two conditions must be met: (1) the liquid pressure inside the blister cavity must be zero, as suggested by Martin, et al.¹⁰ or (2) the liquid pressure p is present, as suggested by Funke² in the case of osmotic blistering. However, in order to maintain a constant moment at the blister tip at all times during the blister growth, the liquid pressure p inside the cavity must reduce continuously with increas-

ing r to meet the requirement of $p \cdot r^2 = \text{constant}$ (cf. equation (2)). Since the likelihood of condition (2) being met is exceedingly small, it is believed that the non-osmotic blister growth consistent with condition (1) can explain the steady-state data in a satisfactory fashion. However, the present model should be valid for both non-osmotic and osmotic blisters that are formed by the cathodic half-cell reactions of coated steel exposed to salt environments.

Another feature of the theory was the prediction of the existence of a non-zero threshold velocity below which the blister cannot grow in steady-state. It is tempting to argue that the non-zero value is an artifact, and its logical value should be zero. However, it should be pointed out that this nonvanishing value actually comes from the first and second law of thermodynamics. As we may recall, in order to activate the steady-state blister growth by stress-assisted mass diffusion, thermal energy dissipation proportional to the quantity $\int J \cdot \nabla \mu \, dx$ (these terms have the same meaning as those given in equation (4)) must have occurred. Thus, in order to have blister growth, a finite velocity is required to supply this entropy at the minimum level. The fundamental physics of blister growth is similar to the case of high temperature diffusive crack growth along a grain interface where proof of the existence of a non-zero threshold velocity had been provided.²⁵

Our theory, based on equations (17-18), suggests that the two materials parameters, σ_f and E , play an important role in the formation and growth of cathodic blisters of painted steel. It is worthwhile to discuss the effects of these parameters on the growth of a blister formed when a painted steel panel is exposed to a salt solution. The information should provide a technical base for designing better protective coatings.

Significance of σ_f

For blister formation on a coating system exposed to an aqueous environment, the coating should still adhere to the substrate beyond the periphery of the blister base. On the other hand, in order for a blister to grow, the bonding strength at the blister tip between the coating and the substrate must have been weakened to a value below that of the region beyond the blister base. This is supported by the results of Nguyen and co-workers,^{8,23} who found that the peel strength of a stiff epoxy coating ($E = 1.7 \text{ GPa}$) on a sandblasted steel substrate decreased from 1.2 kN/m before exposure to a minimum of 0.7 kN/m after 60 days exposure to an alkaline solution containing 3.5 mass % of NaCl at 50°C . They attributed the loss of adhesion in this region as due to water accumulation at the coating/steel interface. On the other hand, the peel adhesion at the cathodic disbonded region was essentially zero. Further, they found no evidence of a transition zone between the cathodic disbonded and the water-induced adhesion loss regions. Similarly, using a combination of a Kelvin probe apparatus and adhesion test, Stratmann et al.²⁶ were able to show that the mechanical adhesion loss at the base of a cathodic blister is always behind the cathodic disbondment front. Both of these results suggest that the coating/steel interfacial region beyond the cathodic re-

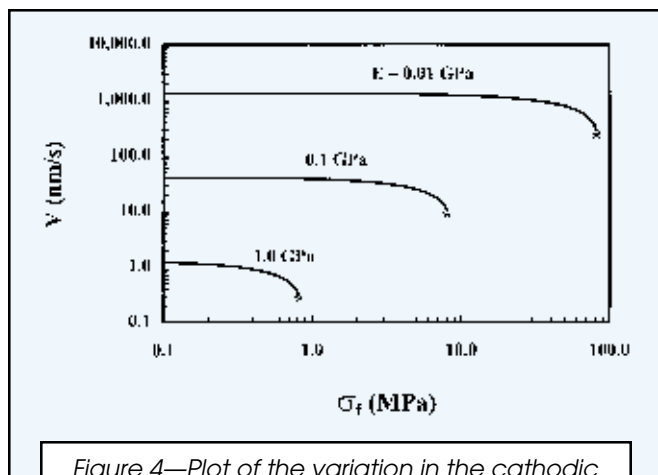


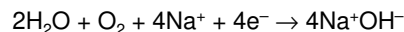
Figure 4—Plot of the variation in the cathodic blistering velocity with respect to the change in σ_f for different values of E ($E = 0.01$ GPa, 0.1 GPa and 1 GPa). Note that "X" marks the points below which the blister will not grow (i.e., no solution is available in real and positive value).

action front is unaffected by the corrosion process, while the bonding strength in the region near a cathodic blister tip is substantially reduced by the corrosion activity.

These results indicate that there is a strong effect of the corrosion process on the disbondment stress at the cathodic blister tip, σ_f . Thus, a knowledge of σ_f above which cathodic blistering does not occur is critical for the development of better protective coatings. Although this value may be difficult to measure experimentally, it can be estimated using the model presented here. Figure 4 displays the relationship, in double logarithmic scale, between σ_f and V (the blister growth rate) for three different types of coatings, ranging from stiff ($E = 1$ GPa) to very flexible ($E = 0.01$ GPa). The curve of this figure was obtained using the values in Tables 1 and 2 for the parameters. The results show that, except for the very high values of σ_f , there is a nearly inverse linear relationship between the blistering rate and disbondment stress at the blister tip for a coating applied to a steel substrate subjected to a corrosive environment. For example, for stiff coatings ($E = 1$ GPa), V decreased from 1.33 nm/s to 0.24 nm/s when σ_f increased from 0.05 MPa to 0.83 MPa. The model also predicts that, for this type of coating, the blister does not grow at all if σ_f is greater than 0.85 MPa. For a very flexible coating ($E = 0.01$ GPa), the blister growth rates increased from 245 nm/s to 1378 nm/s when σ_f decreased from 83.0 MPa to a negligible value of 0.05 MPa. Further, for this very flexible coating, a cathodic blister ceases to grow if σ_f is greater than approximately 85 MPa. The results indicate that by measuring the growth rate of cathodic blistering, the critical coating/substrate bonding strength at which a blister does not expand can be estimated.

The facts that cathodic blisters grow rather quickly during immersion in a salt solution as reported by Martin et al.,^{3,10} indicated that the bonding strength at the tip of a cathodic blister has been considerably weakened so that it can no longer resist the applied bending moment stress. Thus, the main question is what are the factors

that may affect the bonding strength at the tip of a cathodic blister? To better answer this question, one needs to examine the environment at the tip of a cathodic blister. Evan's classical experiment has shown that when a drop of neutral NaCl solution is placed on a bare steel surface, the center of the drop is the anode while the cathodes are located at the periphery.²² This happens because of the greater accessibility of oxygen at the periphery. The same phenomenon occurs when the same salt solution is placed at the defects through the coating of a polymer-coated steel panel. The anodic process takes place at the defect, and the cathodic reactions occur on the metal surface underneath the coating, as indicated earlier. At the cathodic sites, oxygen is reduced, and in the presence of cations, such as Na^+ ions, a highly alkaline NaOH solution is formed at the coating/steel (oxide) interface, following the reaction:



The presence of Na in the cathodic-disbonded areas has been verified by surface analytical techniques.^{26,28} In the previous reaction, the electrons are supplied by the anodic reactions. It is noted that, in order for the corrosion process to occur, there must be a current flow between the anodes and the cathodes. This means that an electrolyte layer must exist at the coating/steel interface within the corrosion cell. In the absence of an external electrical potential applied across the coating, Na^+ ion transport from the defects to the cathodic sites to neutralize the OH^- ions generated at the cathodic sites are believed to be along the coating/substrate interface.^{2,5,26} This electrolyte transport may be enhanced by two effects: potential gradient between the cathode and the anode and the bending stress at the blister tip.

For the first effect, Stratmann et al.²⁴ have found that when corrosion does take place, a strong electrical potential gradient is present between the defects (anodes) and the cathodic sites. They further reported that the cathodic delamination rate increases with an increase in potential gradient.²⁹ A model by Nguyen et al.³⁰ also predicted that Na^+ ion flux to the cathodic blisters increases almost linearly with applied electrical potential between the defect and the cathodic sites. The corrosion-induced potential gradient should accelerate the lateral transport of sodium ions and water from the interior to the cathodic disbondment front. Evidence of electric potential assisted mass transport in coatings is substantiated by several studies. For example, Kittleberger and Elm³¹ have demonstrated that 90% of water uptake into a linseed oil coating was transferred into the coating by the electric potential gradient. Leidheiser⁷ also reported an order of magnitude increase in the transport rate of water in an alkyd coating when the applied potential was increased from open potential (no applied potential) to -0.8 V (versus SCE). Similarly, using Fourier transform infrared spectroscopy in the internal reflection mode, Nguyen et al.³² also showed a substantial increase in the amount of water at the coating/iron interface when the potential was increased from open potential to -2.0 V (versus Pt reference).

The transport of ions would accelerate the flow of water as a result of electroosmosis effect, in which the

flow of counterions in one direction gives rise to a flow of solvent in that direction.³³ Virtually all types of membranes exhibit electroosmosis, which arises by the existence of charged species or by adsorption of charged species in solution onto the walls of the membranes. In corrosion, Sato³⁴ has reported the flow of water accompanying the permeation of Cl^- ions through the rust layer to the occluded pits and crevices. He further indicated that this form of water transport, which is greater than the water diffusion by concentration gradient, provides adequate water for metal ions hydration at the anodes. Water transport by concentration gradient diffusion alone does not provide enough water to sustain localized corrosion of metals. In corrosion of painted steel in electrolytes, the movements of Na^+ ions in the negative-charge cathodic blisters or delaminated areas and Cl^- ions in the positive-charge rusted areas will enhance the transport of water to those regions. This flow of water thus enables Na^+ and Cl^- ions to transport faster than they would otherwise in the absence of water. Therefore, the net current flow between anodes and cathodes should be greater than in the absence of electroosmosis. In summary, both the potential gradient between the defects and cathodic sites and the electroosmosis effect would accelerate the transport of Na^+ ions as well as water to the cathodic blister disbondment front.

The second effect is the bending stress that causes cathodic blistering. This stress should also enhance the flow of electrolyte in the blister to the delamination front. Dickie and co-workers³⁵ have reported that when a static load is applied, the adhesively bonded galvanized steel failed quickly in corrosion environments. They postulated that the applied stress opens up the bonds, permitting the ingress of electrolyte to the cathodic sites.

The presence of the alkaline NaOH solution at the cathodic sites given in the above reaction suggests that the pH in this region should be very high. Indeed, pH as high as 14 has been measured at the cathodic delamination front.³⁶ The strong alkalinity of the white-metal, cathodic disbonded region behind the delamination front has also been verified by a strong violet coloration in a clear coating containing a phenolphthalein pH indicator²⁶ or after spraying with the same indicator over the delaminated area.⁸ The high pH at the cathodic sites, which has been proposed as the main cause for the cathodic disbondment of coating/steel systems, is probably responsible for the decrease of σ_f at the cathodic blister tip. The degree of this corrosion-induced adhesion loss depends on a number of variables, including surface morphology and treatments, the strength of the molecular interaction at the coating/steel interface, and the pH at the cathodic sites. The magnitude of the pH generated is, in turn, a function of the rates of diffusion of oxygen, water, and cations to the cathodic sites, the rate of the OH^- ions diffuses away from the cathodic sites, the potential gradient between the cathode and anode, and the volume of the liquid in the regions where OH^- ions are generated.⁷ Three possible mechanisms have been advocated to explain the loss of coating adhesion due to the presence of cathodic-generated alkaline

products: (1) hydrolysis of the coatings,³⁷ (2) dissolution of the oxide layer,¹ and (3) alkaline-induced debonding at the coating/substrate interface.³⁸ For some coating/steel systems, more than one of these mechanisms is involved, either simultaneously or in stages.⁹ We believe that these mechanisms provide the initial step responsible for weakening the polymer/metal interfacial bond at the blister tip, i.e., reducing σ_f . However, the force liable for expanding the blister size is believed due to the applied bending moment, which may be produced by the in-plane compressive stress of the swollen coating film or by the pressure buildup in the blister cavity, coupled with stress-driven diffusive transport of electrolyte along the coating/metal interface at the cathodic disbondment front.

Significance of E

The cathodic blistering rate is a function of the coatings Young's modulus, E , in the wet state, as given in equations (14-16). It must also take the biaxial stress state into account by using the real E value divided by (1- ν). The relationships between E and V are presented in Figure 5 for $\sigma_f = 0.1, 1.0,$ and 5 MPa . For a coating system having $\sigma_f = 0.1 \text{ MPa}$ of bonding strength at the cathodic blister tip, the blister grows rapidly from 0.2 nm/s at $E = 3 \text{ GPa}$ to 15.2 nm/s at $E = 0.2 \text{ GPa}$. From this analysis, it is clear that, in order to reduce the cathodic blistering rate, coatings having higher E values should be used. This is consistent with practical observation that cathodic blistering generally occurs on flexible polymer films, while cathodic delamination near the defect is noticed for rigid coatings. Note that within the range of E plotted in Figure 5 between 0 and 3 GPa, the solutions for $\sigma_f = 1$ and 5 MPa terminated at the points marked by X as the blister velocities at that point have already reached the threshold values below which the blister is not expected to grow.

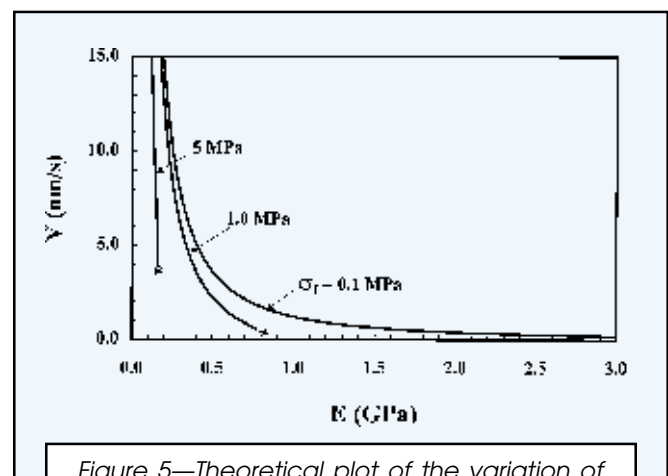
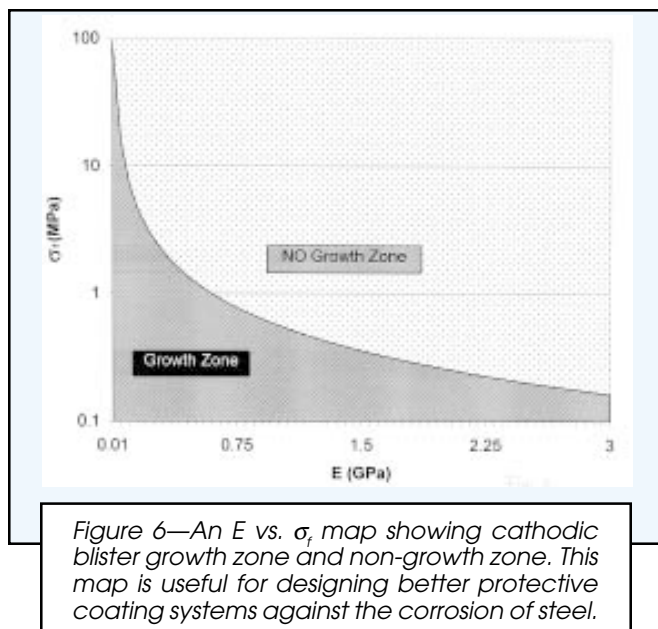


Figure 5—Theoretical plot of the variation of the cathodic blistering velocity as a function of effective Young's modulus, E , for a trio of the disbondment stress, σ_f ($\sigma_f = 0.1 \text{ MPa}$, 1 MPa , and 5 MPa). The mark "X" denotes the points below which real, positive solutions cannot be obtained (i.e., the threshold velocities).



Design Map for Better Coatings Against Cathodic Blistering

Based on results of Figures 4 and 5, we can construct a map aiming at designing better protective coating systems against cathodic blister growth where zones of growth versus non-growth areas in the E - σ_f space are indicated, regardless of the residual stress state in the coating film. Figure 6 shows such a map where a nonlinear border line separating the whole area into two zones: the growth zones is in the lower-left part, whereas the non-growth zone is in the upper-right portion. It should be noted that, strictly speaking in a mathematical sense, the nonlinear border line belongs to the growth zone since this line defines a family of threshold blister growth velocities. For example, the point ($E = 0.1$ GPa, $\sigma_f = 8.1$ MPa) on the line predicts blister growth at a threshold value of $V = 8.98$ nm/s. Figure 6 also reveals that, even for highly flexible coatings, no substantial blistering would occur if σ_f remains high. That is, if the bonding strength of the system is still high during exposure, no significant blisters would develop, even if substantial corrosion has already occurred on the coated panel. This may be achieved through surface treatment of the metallic substrate or chemical modifications of the coatings to provide an alkaline-resistance interface. On the other hand, little change of cathodic blistering will occur if the coating is rigid, even if its wet adhesion to the metal is poor. In this case, the main cathodic-induced mode of degradation is the delamination around the defects, as has been reported widely in the literature, instead of blistering away from the defects. The map shown in Figure 6 is useful to a coating design engineer. If the failure mode is cathodic blistering, then a design against blister growth using properties of the coating systems lied within the upper portion of the map is highly advisable. It is expected that with those properties selected, the blisters in the coating system thus designed will not grow, even if they are initiated. Accordingly, the designed system will be durable and be expected to last a long time.

CONCLUSIONS

Polymer coatings are the most common and economical means to protect metals from corrosion. Despite great advances in coatings technology in the last decade, failure of polymer coatings from corrosive attack by the environment remains a general phenomenon. The service life and the durability of the polymer coating systems are the main concerns of the present paper. Since the blister growth is observed to play an important role in the failure processes, we developed a theory to predict the steady-state blister growth rate for a known driving force, based on stress driven mass transport of electrolytes along the interface between the polymer coating and the steel substrate. In the theory, the coating is modeled as a cantilever beam subjected to a bending moment applied at the blister tip. A boundary value problem is formulated wherein Fick's law of mass diffusion is satisfied along the coating/metal interface, and the principles of the strength of materials are obeyed in the beam. The outcome is a governing fifth order ordinary differential equation for the "deflection" of the beam, together with appropriate boundary conditions at both ends of the beam. Solving the boundary-value problem mathematically, we obtained a unique solution for the blister growth, which can be cast in the form of nonlinear functional relationship between the blister propagation rate and the applied moment at the tip. Given the bending moment at the blister tip, the present theory is capable of predicting how fast the blister will grow in steady-state, or not grow at all, if the system's materials constants are known.

Stating in physical terms, it can be said that the driving force leading to blister growth is the applied moment induced by the in-plane compressive stress of the swollen "buckled" film or by the pressurized stresses imposed by the solution present inside the blister cavity. The theory is confirmed by the good agreement between the predicted blister growth velocity and the experimental data measured on a paint coated steel panel immersed in a 5 mass% saltwater solution. Furthermore, besides the quantitative prediction of a nonlinear functional relationship between the blister growth rate and the applied bending moment, the theory also predicts a threshold moment below which the blister will not grow. Thus, if one can make sure the actual moment present at the blister tip will not exceed this threshold value, say, for example, via the processing route prior to service, then the life of the coating system can be expected to lengthen significantly. We also explored the role of disbondment stress and coating stiffness in the blister growth behavior. We found that increasing the disbondment stress will reduce the blister growth rate monotonically in a nonlinear fashion. Similarly, increasing the coating stiffness even retards the blister growth more drastically. A blister growth map has been constructed where non-growth region in the space of coating Young modulus/disbondment stress parameters has been identified in which blisters, even if initiated, will not propagate. It is expected that the current theory will assist coating formulators in designing an optimum condition on the physical and mechanical properties of the selected coating system.

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