

A non-osmotic blister growth model in coating systems

T.-J. Chuang

Ceramics Division, National Institute of Standards and Technology, Gaithersburg, Md., USA

T. Nguyen

Building Materials Division, National Institute of Standards and Technology, Gaithersburg, Md., USA

ABSTRACT: A blister growth model is proposed for a coating system consisted of a polymer film applied to a steel substrate exposed to salt solutions. The blister is considered to grow at a constant rate between the coating and the rigid steel substrate. 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 at the delamination front. The driving force leading to blister growth is the applied bending moment induced by the in-plane compressive stress of the swelling "buckled" film. 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", and 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 5% salt water solution.

1 INTRODUCTION

The use of organic 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 wherever corrosion of metals will occur under polymer coatings. 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 coated panels are exposed to a salted environment. This phenomenon is often observed on metal objects with or without apparent damaged 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 models for quantifying the growth of a cathodic blister. This study presented a model to predict the growth rate of cathodic blisters when coated steel is exposed to salt water.

Cathodic blister initiation is always associated with some form of defects in the coatings, such as artificial scribed mark (Martin et al. 1990), small pores (Funke, 1985), or conductive pathways developed during exposure (Nguyen et al. 1996). Defects allow channels for ions transport from the environment to the metal surface, where corrosion reactions will take place

on the metal surface at and around the defects. Corrosion products generated by the cathodic reactions reduce substantially the coating/metal bond strength at these sites (cathodic sites), creating blister nuclei. These sites are formed at or away from the defects depending on the size of the defects. The details of a cathodic blister initiation site and its location are stochastic in nature. It may be an imperfection or weakness in the coating/substrate bonds, a microvoid at the coating/substrate interface, or a defect on the substrate surface. Regardless of the location, an incubation time is always required for the initiation of a cathodic blister on a polymer-coated steel panel. For panels containing no apparent defects or small pores, the time it takes for blisters to occur is much longer for panels contain large defects.

The issue of cathodic blister growth is subjected to debate. There are generally two schools of thought with regards to the driving force. Funke (1985) believed that osmotic pressure is the main mechanism responsible for the growth of a cathodic blister. But in some cases, it is clear (Martin, et al. 1990) that after the blister is formed, a bending moment is set up at the periphery or "tip" of the blister in the film 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, rather, it is from the bending moment present inside the coating, it is called non-osmotic disbondment or blister growth.

The present paper adopts the concept of the latter 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 at a (unknown, a priori) constant velocity driven by the applied bending moment at the periphery. Under the action of an applied bending moment, the cathodic reaction-containing liquid is driven laterally along the coating/substrate interface to the delamination front from the blister pool, causing the coating to deform. The Fick's law in diffusion links this deflection field with the distributed loads along the beam length. By considering the coating as a semi-double cantilever beam, 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 moment, ambient temperature, film thickness, elastic, and diffusive properties. In the discussion section, we test the applicability of the present theory using experimental data given by Martin et al. (1990) in which blister growth rates were measured for an alkyd primer/top coat system applied to a sandblasted steel substrate immersed in a 5% salt solution at room temperature. The agreement between the theory and data shows a promising prospect for the present model.

2 BLISTER INITIATION

Prior to placing into service, a coating/substrate system is usually pre-cured at a higher temperature, e.g., 70°C, thereby introducing a tensile in-plane residual stress in the coating. This stress level can be as high as 15 MPa (Martin et al. 1990). When the coated panel is immersed in a water solution containing salt, water gradually diffuses into the coating causing swelling with a volume expansion. The swelling-induced in-plane stress is so high that can change the residual stress state from 15 MPa in tension into 5 MPa in compression. During exposure, randomly distributed pores are formed in the coatings films, which provide conductive pathways for ions to reach the metal surface. Once ions arrive the metal surface, an electrochemical cell is established where iron is consumed at the anodes and oxygen is reduced to form hydroxyl ions at the cathodes. The generated hydroxyl ions cause a disbondment of the coating from the substrate. When the size of the disbonded area reaches

a critical size, buckling of the coating due to the compressive stress occurs, resulting in the formation of the blister.

If w is the buckling distance (i.e., the height of the blister), then a bending moment M_o per unit length of the blister circumference will be introduced at the "tip" of the blister due to the residual compressive stress σ_r :

$$M_o = \sigma_r h w \quad (1)$$

where h is the thickness of the coating, including primer and topcoat. Moreover, if we let σ_f be the cathodic disbondment stress, where σ_f is defined as the tensile strength of the interface below which coating does not separate from the substrate, then at the blister tip where regions of failed and unfailed bonding are separated, the interfacial stress σ_o must always be the disbondment stress σ_f , which is a material constant, namely,

$$\sigma_o = \sigma_{yy}(0) = \sigma_f \quad (2)$$

where subscript o denotes tip location, namely $\sigma_o = \sigma(0)$.

3 BLISTER GROWTH

Once the blister is initiated, it can grow slowly at a steady state velocity V under the action of the applied bending moment M_o located at the periphery of the blister. The present paper aims to predict V as a function of M_o , materials properties, and temperature, so that ultimately the service life of the coating system can be estimated. In order to achieve this goal, a mathematical model is formulated in which Fick's laws and principle of strength of materials are injected to form a well-defined boundary value problem. Those tasks are described in details in the following subsections.

3.1 Liquid transport at interface

Consider mass transport of liquid (electrolyte in this case) along the coating/steel interface at the cathodic delamination front ahead of the blister tip (see Figure 1). When the radius of the blister is large enough, plane-strain conditions in steady state prevail, because the radius of curvature of the periphery in the x - z plane 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. We can then consider the tip as a straight tip

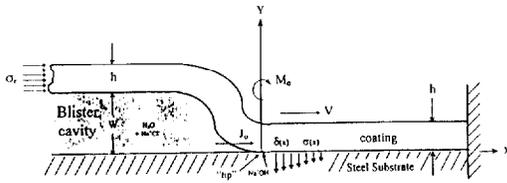


Figure 1. Schematic of the blister growth model

front along the z-axis moving at a velocity V in the x direction with a moving coordinate system with its origin attached to the tip.

The chemical potential at any location in the 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 in the interface. Fick's law then dictates that the diffusive flux be in inverse proportion to the gradient of the chemical potentials. Thus,

$$J(x) = -\frac{D_b \delta_b}{kT \Omega} \nabla \mu(x) = \frac{D_b \delta_b}{kT} \frac{d\sigma}{dx} \quad (3)$$

where J is the matter flux, $D_b \delta_b$ is the interfacial diffusivity 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 $J(0) = J_0 = wV/\Omega$. Combination with Equation (3) then gives

$$\sigma_o' = \frac{w kT V}{D_b \delta_b \Omega} \quad (4)$$

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

3.2 A semi-double-cantilever beam model

Consider a semi-double-cantilever beam located along the positive x -axis with a unit thickness in the z -direction as sketched in Figure 1. The blister is located at $x \leq 0$, and the tip at $x=0$ is moving at a constant speed V in the positive x -direction. The beam is subjected to a bending moment M_0 applied at $x=0$. If we express local deflection of the beam as $\delta(x)$ and local externally applied stress to the beam as $\sigma(x)$, then the principle of the "strength of materials" demands that they must be related by the following equation for the beam:

$$\frac{Eh^3}{12(1-\nu^2)} \frac{d^4 \delta}{dx^4} + \sigma(x) = 0 \quad (5)$$

for $x \geq 0$. Here E is Young's modulus of the coating

obtained in the wet (water immersion) state, ν is Poisson's ratio of the coating, and h is the total coating thickness. Meanwhile, at an arbitrary location x , under steady state conditions the local deflection must be related to the flux as $\delta(x) = \Omega J(x)/V$ due to mass conservation requirement. Thus, after combining with equation (3), we have

$$\delta(x) = \frac{D_b \delta_b \Omega}{kT V} \frac{d\sigma}{dx} \quad (6)$$

Upon substituting Eq.(6) into Eq.(5) to eliminate the stress variable, we finally arrive at a fifth order differential equation for the unknown local deflection $\delta(x)$ of the beam:

$$L^5 \frac{d^5 \delta}{dx^5} + \delta = 0 \quad (7)$$

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

$$L = \left[\frac{Eh^3 D_b \delta_b \Omega}{12(1-\nu^2) V kT} \right]^{1/5} \quad (8)$$

The boundary conditions at the blister tip are as follows:

$$-\frac{Eh^3}{12(1-\nu^2)} \delta_o^{(IV)} = \sigma_o \quad (9)$$

according to Equation (2), and, furthermore,

$$-\frac{Eh^3}{12(1-\nu^2)} \delta_o^{(V)} = \sigma_o' \quad (10)$$

according to Equation (4). Here the superscripts (IV) and (V) denote fourth and fifth derivatives respectively. Moreover, the shear stress at the tip must vanish. This means that

$$\delta_o^{(III)} = 0 \quad (11)$$

The differential equation (7), together with the boundary conditions (9-11) forms a well-defined boundary value problem so that a unique solution is guaranteed. This mathematical problem has been solved by Chuang (1975), and the solutions can be expressed as a function of 3 functions superimposed together: exponential; exponential times sines and

exponential times cosine functions. Plots of the solutions along the 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 finally are able to express M_o at the tip as

$$M_o = L^3 \sigma_o' + \frac{1+\sqrt{5}}{2} L^2 \sigma_o \approx L^3 \sigma_o' + 1.62 L^2 \sigma_o \quad (12)$$

Substituting the expressions for L in Eq.(8), σ_o' in Eq. (4) and σ_o in Eq. (2) into Eq. (12), we obtain the relationship between the applied moment at the tip and the steady-state blister growth rate:

$$M_o = A \cdot V^{\frac{2}{5}} + B \cdot V^{-\frac{2}{5}} \quad (13)$$

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

$$A = \frac{w}{\Omega^{2/5}} \left[\frac{kT}{D_s \delta_b} \right]^{\frac{2}{5}} \left[\frac{Eh^3}{12(1-\nu^2)} \right]^{\frac{3}{5}} \quad (14)$$

$$B = 1.62 \sigma_f \left[\frac{Eh^3 D_s \delta_b \Omega}{12(1-\nu^2) kT} \right]^{\frac{2}{5}} \quad (15)$$

A close examination of Equation (13) indicates that there is a threshold bending moment $(M_o)_{th}$ below which the blister will cease to grow:

$$(M_o)_{th} = 2\sqrt{AB} = 0.73 \sqrt{\frac{Ew\sigma_f h^3}{1-\nu^2}} \quad (16)$$

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

$$V_{min} = \left(\frac{B}{A} \right)^{\frac{5}{4}} = 1.83 \left(\frac{\sigma_f}{w} \right)^{\frac{5}{4}} \left[\frac{D_s \delta_b \Omega}{kT} \right] \left[\frac{Eh^3}{12(1-\nu^2)} \right]^{-\frac{1}{4}} \quad (17)$$

below which the blister will not grow. Equation (13)

can be written in a non-dimensional form in terms of the normalized moment, m and the blister growth velocity, v :

$$v = \left[m + \sqrt{m^2 - 1} \right]^{\frac{5}{2}} \quad (18)$$

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 moment respectively. Figure 2 plots the predicted blister growth velocity as a function of bending moment applied at the tip. Now, Martin, et al.(1990) has estimated a critical moment for blister initiation which has the following form:

$$M_{mi} = 3 \frac{Eh^3 w}{a^2} \quad (19)$$

where a is the diameter of the blister nuclei at the initiation. It is interesting to compare the bending moment levels of Equations (16) and (19). For instance, if the moment predicted by Equation (16) is less than Equation (19), then the blister will not grow even if it is initiated. On the other hand, if the value calculated by Eq. (16) is larger than by Eq. (19), the blister will grow after its formation.

4 COMPARISON WITH EXPERIMENT

In order to test the validity of the proposed blister growth model, data collected from the experiment performed by Martin, et al. (1990) are used for the prediction. Table 1 lists the relevant material properties

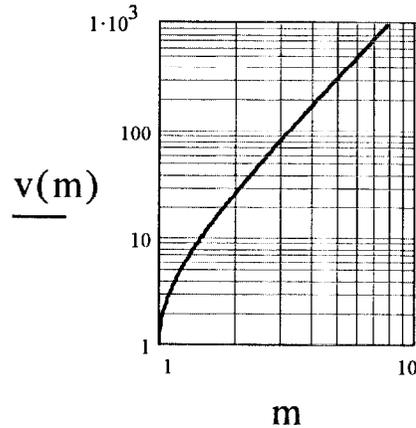


Figure 2. Functional relationship between v and m

Table 1. Values of E , ν , w and σ_f

$E(\text{GPa})$	ν	$h (\mu\text{m})$	$w(\text{mm})$	$\sigma_f(\text{MPa})$
1.0	0.37	145.0	3.0	-5.0

Table 2. Values of $D_b\delta_b$, σ_f and Ω

$D_b\delta_b(\text{m}^3\text{s}^{-1})$	$\sigma_f(\text{MPa})$	$\Omega(\text{m}^3)$	$T(\text{K})$
2×10^{-13}	0.1	10^{-29}	300

Table 3. Applied bending moment and predicted and observed blister growth velocities

$M_0(\text{N}\cdot\text{m}/\text{m})$	$V_{\text{predicted}}(\text{nm}/\text{s})$	$V_{\text{measured}}(\text{nm}/\text{s})$
2.18	1.28	1.86

that are measured, or estimated from data given, by Martin, et al. (1990) and Table 2 provides the other material constants, which were not included in the experiment; they were obtained from open literature. $D_b\delta_b$ was taken from Pommersheim and Nguyen data (Pommersheim & Nguyen, 1995), σ_f was approximated from peel strength results given by Nguyen and Martin (1996) and data on tensile stress and peel strength of polymer/substrate bonds provided by Kinloch (1975), and Ω value was given by King (1970).

Table 3 presents the calculated applied bending moment at the tip (Eq. 12), the predicted blister growth velocity as given by Eq. (18), and the observed velocity given by Martin et al (1990).

It is evident from Table 3 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 0.53 N·m/m, which is about one-quarter of the applied bending moment, and the minimum steady-state blister growth velocity is 0.05 nm/s, which is about thirty 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 $a=5$ mm, then the initiation moment required as computed from Eq. (19) is 0.55 N·m/m, which is larger than the threshold level for growth. This means that once the blister is formed, the present theory predicts that the blister will start to grow after initiation.

5 DISCUSSION

Eqs. 13 - 15 indicate that the two materials parameters, σ_f and E , play an important role in the formation and

growth of blisters of polymer-coated steel. This section discusses the effects of these two parameters on the growth of a blister formed when a polymer-coated steel panel is exposed to a salt solution. The information should provide a technical base for designing better protective coatings.

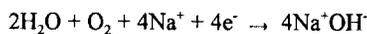
5.1 Significance of σ_f

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 between the coating and the substrate at the tip of the blister must be weaker than the unbroken bonds in the interior. This is supported by the results of Nguyen and Martin (1996), who found that the peel strength of a strong and tough epoxy coating ($E=1.7\text{GPa}$) on a sand-blasted 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 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 delamination front was substantially lower, approximately 0.1 kN/m (Alshed et al. 1994). Further, there is no transition between the cathodic-induced delamination front and the water-induced adhesion loss region. Similarly, using a combination of a Kelvin probe apparatus and adhesion test, Stratmann et al. (1989) were able to show that the mechanical adhesion loss at the base of a blister is always behind the cathodic delamination front. Both of these results suggest that the interfacial region beyond the cathodic reaction front is unaffected by the corrosion process, while the interfacial bonding strength at the tip of a cathodic blister is substantially reduced by the corrosion activity.

The above discussion indicates 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. Eqs. 13-17 of the model presented here can be used to obtain this value. The relationship in double logarithmic scale between σ_f and V (the blister growth rate) is displayed in Figure 3 for three different types of coatings, ranging from tough ($E=1\text{GPa}$) to very flexible ($E=0.01\text{GPa}$). This figure was obtained using values given 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 rather strong 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 0.84 MPa. For a 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 83 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 exposure to a corrosive environment (Martin et al. 1990) indicated that the bonding strength at the tip of a cathodic blister has been weakened 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 that question, one needs to examine the environment at the tip of a cathodic blister. Evans (1945) classical experiment has shown that when a drop of 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. 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 take 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:



In the above 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 anode and the cathode. This means that there must be an electrolyte layer exists at the coating/steel interface within the corrosion cell. In the absence of an external electrical potential applied across the coating, Na^+ ions transport are believed to be along the coating/steel interface. Further, when corrosion occurs, a strong potential gradient exists between the defect and the cathodic sites. This potential gradient accelerates the transport of Na^+ ions

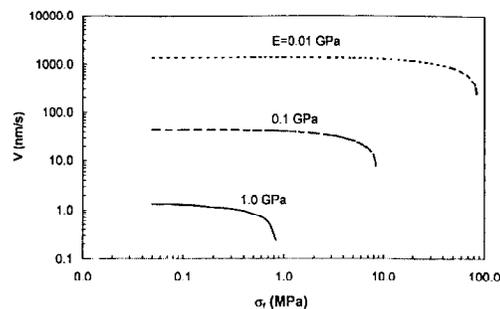


Figure 3. Relationship between σ_f and V for different values of E .

from the defects to the cathodic regions (Starmann, 1994). In addition, Na^+ ions flow also probably produces a potential gradient, similar to that when Cl^- ions permeate to the anodic areas (Sato 1987). Both the corrosion- and Na^+ flow-induced potential gradients should accelerate the lateral transport (electroosmosis) of water and the corrosion fluid from the blister periphery to the cathodic delamination front. This electroosmosis transport was demonstrated by Kittleberger and Elm (1945), who showed that 90 % of water uptake into a linseed oil coating was transferred into the coating by the electrical potential gradient. Further, the bending moment stress that causes blistering should also enhance the flow of electrolyte in the blister to the delamination front. All these transport-assisted factors may explain for the high diffusion coefficient value of Na^+ along the coating/steel interface obtained by Pommersheim and Nguyen (1994).

The presence of the alkaline NaOH solution at the cathodic delamination front 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 (Ritter and Kruger, 1983). This high pH at the cathodic sites, which has been proposed as the main cause for the cathodic disbondment of coating/steel systems (Leidheiser, et al. 1983), is probably mostly responsible for the decrease of σ_f at the cathodic blister tip. The degree of 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 delamination front. 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.

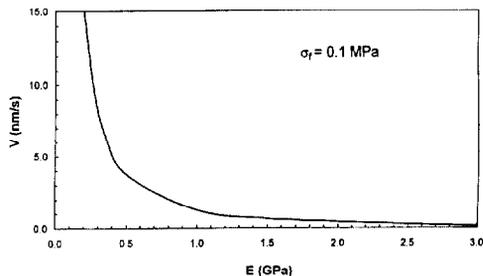


Figure 4. Relationship of V vs. E for $\sigma_f = 0.1$ MPa

Three possible mechanisms have been advocated to explain for the loss of coating adhesion due to the presence of cathodic generated alkaline products: 1) hydrolysis of the coatings (Dickie, 1986), dissolution of the oxide layer (Leidheiser, 1983), and 3) alkaline-induced debonding at the coating/substrate interface (Koeler, 1985). For some coating/steel systems, more than one of these mechanisms is involved, either simultaneously or in stages (Watts, 1989).

5.2 Significance of E

The cathodic blistering rate is a function of the coatings Young modulus in the wet state, as given in Eqs. 13-15). The relationship between E and V is presented in Figure 4 for $\sigma_f = 0.1$ MPa. For a coating system having this level of bonding strength at the cathodic blister tip, the blisters grow rapidly from 0.2 nm/s at E = 3 GPa to 15.2 nm/s at E = 0.2 GPa. From this analysis, in order to reduce the cathodic blistering rate, coatings having higher E values should be used. This is consistent with practical observation for the epoxy-coated steel reinforcing bar industry, where stiffer coatings are preferred because they perform better.

6 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, polymer coatings lose their protective properties and corrosion under coatings do occur. One of the most severe degradation modes of coated steel exposed to salt water is the cathodic blistering. If the effectiveness of protective coatings is to be increased, it is essential to develop models for quantifying the degradation process. This study presented a model to predict the growth rate of blisters formed by the corrosion process. The driving force leading to blister

growth is the applied bending moment induced by the in-plane compressive stress of the swelling "buckled" film. The predicted blister growth velocity compared favorably with the experimental observations on a paint coated steel panel immersed in a 5% salt water solution.

REFERENCES

- Alsheh, D., Nguyen, T., and Martin, J.W., 1994, Proc. Adhesion Society Meeting, Orlando, FL, February, 1994, p.209.
- Chuang, T.-J., 1975, Models of Creep Crack Growth by Coupled Grain Boundary and Surface diffusion, Ph.D. Thesis, Brown University, Providence, RI.
- Dickie, R.A., 1986 in "Polymeric Materials for Corrosion Control," Dickie, R.A. and F.L. Floyd, F.L. (Eds.), *Am. Chem. Soc. Symposium Series 322*, Am. Chem. Soc., Washington, D.C., p.136.
- Funke, W., 1985, *Ind. Eng. Chem. Prod. Res. Prod. Dev.*, 24, 343.
- King, H.W., 1970, in Physical Metallurgy, Ed. R.W. Cahn. North Holland, Chapter 2.
- Kittelberger, W.W. and Elm, A.C., 1946, *Ind. Eng. Chem.* 38, 695.
- Koehler, E.L., 1985, *J. Electrochem. Soc.*, 32, 1005.
- Leidheiser, H., Jr., Wang, W. and Igetoft, L., 1983, *Prog. Org. Coat.*, 11, 19.
- Martin, J.W., McKnight, M.E., Nguyen, T., and N. Embree, E., 1989, *J. Coatings Technol.*, 61, No.772, 39.
- Martin, J.W., Embree, E. and Tsao, W., 1990, *J. Coatings Technol.*, 62, No.790, 25.
- Nguyen, T. and Martin, J. W., 1996, in Durability of Building Materials and Components, Ed. C. S. Jostons, EXFN SP on, Vol. P.491.
- Pommersheim, J. Nguyen, T., 1995, Cations Diffusion at the Polymer Coating/Metal Interface, *J. Adhesion Sci. and Technol.*, 9, 935.
- Ritter, J.J., and Kruger, J., 1981, in "Corrosion Control by Organic Coatings," Leidheiser, H., Jr., (Ed.), Natl. Assoc. Corros. Eng., Houston, TX, p.28
- Sato, N., 1987, *Corrosion Sci.*, 27, 421.
- Stratmann, M., Feser, R., and Leng, A., 1994, *Electrochimica Acta*, 39, 1207.
- Watts, J.F., 1989, *J. Adhesion*, 31, 73.