

fact that the delamination area after a cyclic corrosion test did increase with an increase in the calculated total cross-sectional area of pores.

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# Determination of Coating Deterioration with EIS

## I. Basic Relationships

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## ABSTRACT

Various parameters that can be obtained from impedance data such as the break-point frequency  $f_b$ , the magnitude of the phase angle minimum  $\Phi_{min}$  at high frequencies, and the frequency  $f_{min}$  of  $\Phi_{min}$  are useful to estimate the degree of deterioration of organic coatings on metals. Data obtained earlier by Kendig and Mansfeld for polybutadiene on steel have been reinterpreted using this concept. The delamination function defined in this paper based on impedance data agrees very well with the degree of delamination determined visually according to ASTM D 610.

**KEY WORDS:** break-point frequency, electrochemical impedance, pore resistance, delamination, polybutadiene coating

## INTRODUCTION

One of the most successful applications of electrochemical impedance spectroscopy (EIS) has been in the evaluation of the corrosion behavior of polymer coated metals. Kendig and Mansfeld have used the equivalent circuit shown in Figure 1 to analyze im-

pedance spectra obtained for steel and Al alloys coated with polybutadiene.<sup>1-4</sup> The effect of different pretreatments for steel on the resulting corrosion resistance of the coated steel during exposure to NaCl was characterized by the time dependence of the parameter  $R_{po}$  (Figure 1), which was called "the pore resistance".<sup>1-4</sup> Large differences were observed for different surface pretreatments (Figure 2), and it was argued that for less corrosion-resistant surfaces, the accumulating corrosion products would produce mechanical pressure on the coating, which in turn would produce additional defects and decrease the experimental values of  $R_{po}$ .<sup>1-4</sup>

Recently, Haruyama et al. suggested that the decrease of  $R_{po}$  with exposure time is due to an increase of the delaminated area  $A_d$  according to<sup>5</sup>

$$R_{po} = R_{po}^0 / A_d \quad (1)$$

$$\text{where } R_{po}^0 = \rho d \text{ (ohm}\cdot\text{cm}^2) \quad (2)$$

In this approach, it is assumed that coating properties such as the resistivity  $\rho$  do not change with exposure time. Following this concept (Equation [1]), it becomes clear that the experimental values of the polarization resistance  $R_p$  and the electrode capacitance  $C_{dl}$  of the delaminated area will also change as

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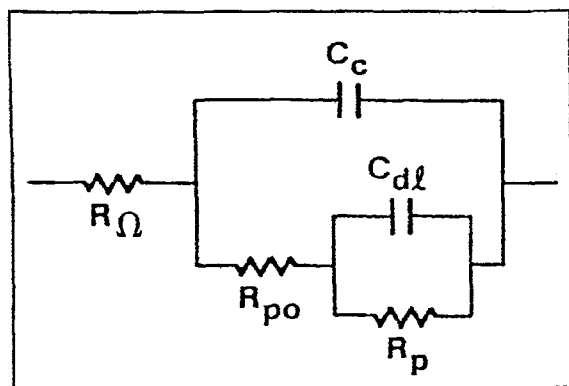


FIGURE 1. Equivalent circuit for the corrosion behavior of a polymer-coated metal.

coating delamination increases

$$R_p = R_p^o / A_d \quad (3)$$

$$C_{dl} = C_{dl}^o A_d \quad (4)$$

with the characteristic values  $R_p^o$  (of  $\text{m}\cdot\text{cm}^2$ ) and  $C_{dl}^o$  ( $\mu\text{F}/\text{cm}^2$ ).

In Equations (3) and (4), it is assumed that the delaminated area  $A_d$  equals the corroding area  $A_{\text{corr}}$ . For transparent coatings such as polybutadiene, it has been observed that  $A_d$  is usually somewhat larger than  $A_{\text{corr}}$ .<sup>1-3</sup> The definition of  $A_d$  used here corresponds to that of ASTM D 610.

The coating capacitance  $C_c$  ( $\mu\text{F}$ ) depends only on the total sample area  $A$ :

$$C_c = (\epsilon\epsilon_0/d) A = C_c^o A \quad (5)$$

where  $d$  is the thickness of the coating and  $\epsilon$  its dielectric constant.

Haruyama et al. have suggested that the extent of delamination can be determined experimentally from the break-point frequency  $f_b$ , which—using certain simplifying assumptions—is given by<sup>5</sup>

$$f_b = 1/2 \pi R_{po} C_c = (1/2 \pi R_{po}^o C_c^o) A_d/A = f_b^o A_d/A = f_b^o D \quad (6)$$

where

$$D = A_d/A = f_b/f_b^o$$

is the delamination ratio. The parameter  $f_b^o$ , which corresponds to the break-point frequency for a totally delaminated coating ( $D = 1$ ), depends only on the coating parameters  $\epsilon$  and  $\rho$  and is independent of coating thickness:

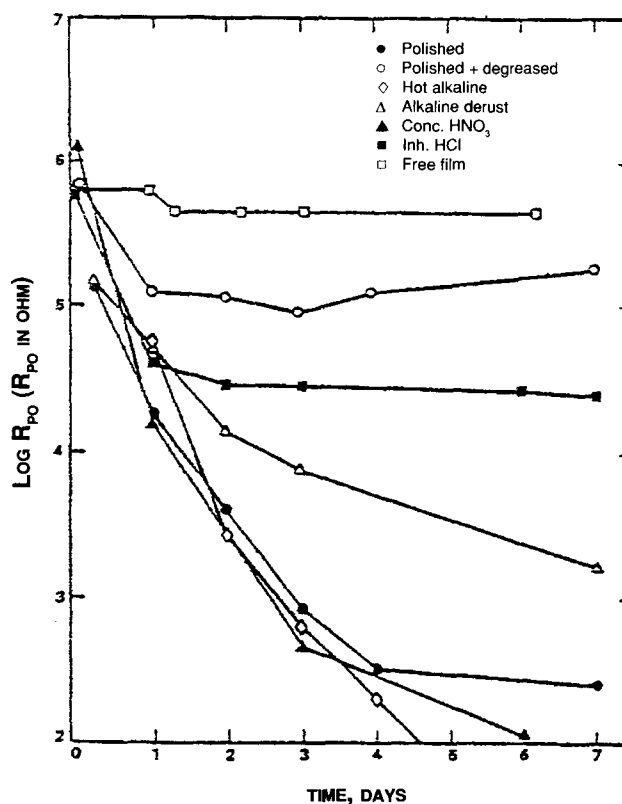


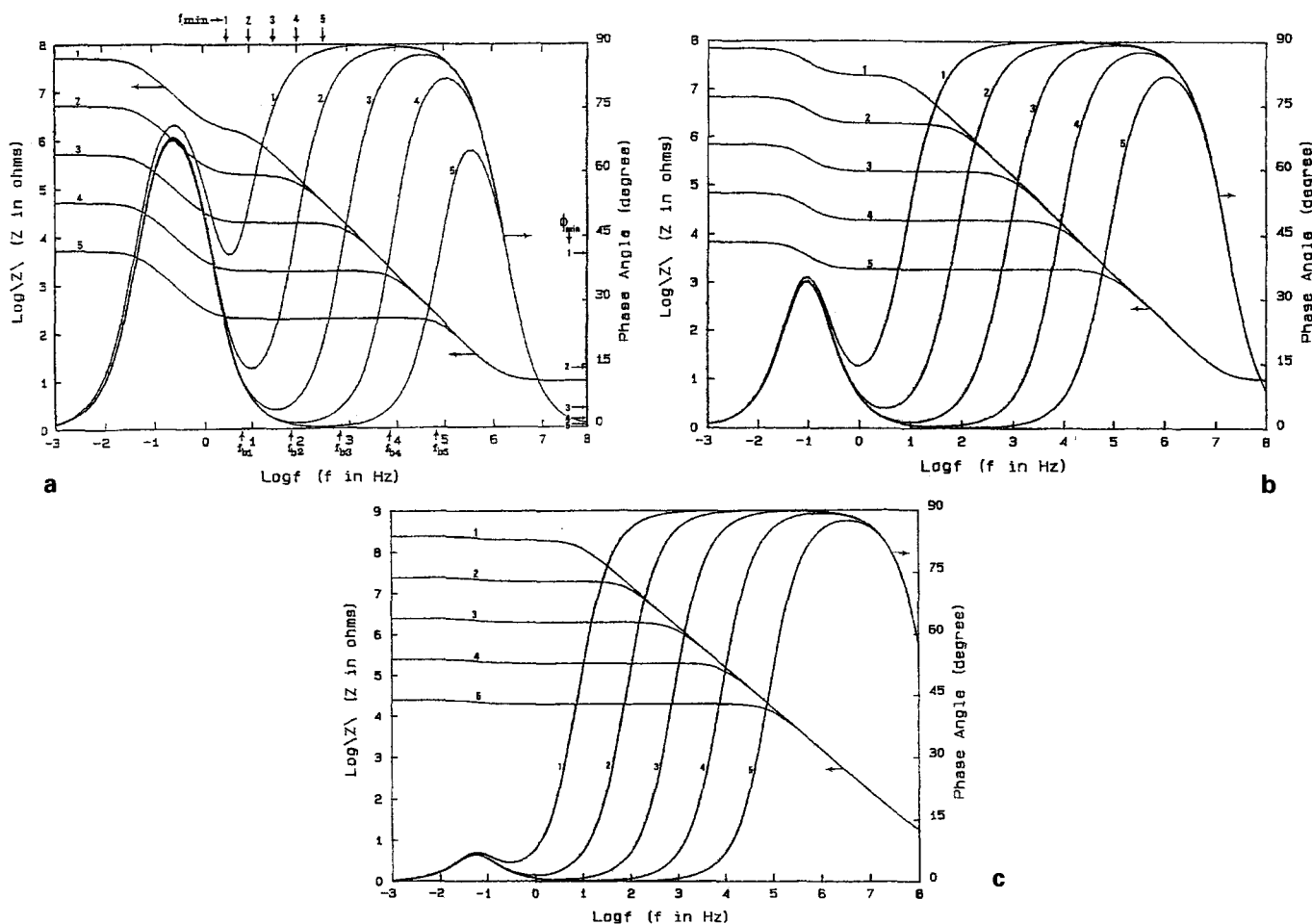
FIGURE 2. Time dependence of  $R_{po}$  for coated steel with different surface pretreatment procedures and for a free film ( $A = 20 \text{ cm}^2$ ).<sup>2</sup>

$$f_b^o = 1/2 \pi \epsilon \epsilon_0 \rho \quad (7)$$

The break-point frequency is defined as the frequency at which the phase angle reaches 45 degrees.<sup>6</sup> Figure 2 is essentially a plot of  $\log(1/f_b)$  vs time since  $C_c$  can be considered to remain constant (Equation [6]).

In considering the use of the break-point frequency for determination of the delaminated or corroded area, one has to consider that both  $\epsilon$  and  $\rho$  in Equation (7) are expected to change with increasing exposure time. Due to water uptake of the coating,  $\epsilon$  will increase while  $\rho$  will decrease as conductive paths and defects develop in the coating.<sup>1-4</sup> In Equation (7),  $f_b^o$  is therefore not a constant value, but has to be expected to depend on exposure time. This problem will be discussed in more detail in Part II of this paper.<sup>9</sup>

There are additional parameters that can be obtained with EIS and can be used to follow the time dependence of coating delamination and to determine the values of  $D$  using certain assumptions. In addition, the delamination function  $\Delta$  will be introduced, which is the electrochemical equivalent of the value DEL that is determined visually according to ASTM D 610. A re-



**FIGURE 3.** Theoretical impedance plots for different degrees of delamination  $D = 10^{-4}$  (curve 1),  $10^{-3}$  (2),  $10^{-2}$  (3),  $10^{-1}$  (4), and 1 (5) and different coating thicknesses  $d = 10 \mu\text{m}$  (a),  $100 \mu\text{m}$  (b), and  $1000 \mu\text{m}$  (c).  $A = 32 \text{ cm}^2$ .

interpretation of the data by Kendig and Mansfeld (Figure 2), according to this concept, will be given.

### MODELING OF EIS DATA FOR COATING DELAMINATION

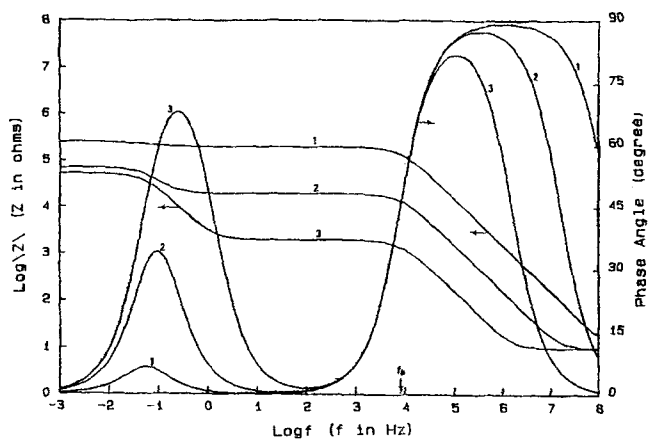
Theoretical impedance spectra, according to the model in Figure 1 and Equations (1) through (5), are shown in Figures 3(a) through (c) for coating thicknesses of  $d = 10 \mu\text{m}$  (Figure 3[a]),  $100 \mu\text{m}$  (Figure 3[b]), and  $1000 \mu\text{m}$  (Figure 3[c]) using the coating parameters  $C_c = 1.02 \times 10^{-7}/d \text{ F}$  ( $d$  in  $\mu\text{m}$ ),  $\rho = 6.27 \times 10^6 \text{ ohm}\cdot\text{cm}$ , and  $C_{dl}^o = 2 \times 10^{-5} \text{ F/cm}^2$ . The spectra have been calculated as functions of the delamination ratio  $D$  in a range between  $10^{-4}$  and 1. As can be seen by a comparison of the three figures, very little delamination (e.g., 0.01 percent in Figure 3[a]) causes large changes in the spectra and the appearance of two time constants for thin coatings. On the other hand, for very thick coatings, it is difficult to detect the occurrence of the second time constant at low frequencies (Figure 3[c]).

Four break-point frequencies can be detected in the spectra of Figure 3(a). The break-point frequency  $f_b$ , as defined in Equation (6), is independent of coating thickness and has the same values for a given degree of delamination  $D$  for all three cases (Figures 3[a] through [c]). Figure 4 shows the spectra for  $D = 0.1$  for the three thickness values. While  $f_b$  is constant, the magnitude and frequency of the maxima and minima of the phase angle at intermediate and low frequencies depend on coating thickness.

In addition to  $f_b$ , it is also possible to use the minimum of the phase angle  $\Phi_{\min}$  and its frequency  $f_{\min}$  to characterize the extent of delamination (Figures 3[a] and 4). This approach is especially useful for thinner coatings. The analytical relationships between  $\Phi_{\min}$  and  $D$  and  $f_{\min}$  and  $D$  are quite complicated. However, the results in Figures 5(a) through (c) that were calculated for the equivalent circuit in Figure 1 as a function of  $D$  and  $d$  show that the following relationships apply:

$$\log f_b = a_1 + b_1 \log D = a_1 + \log D \quad (8)$$

$$\log f_{\min} = a_2 + b_2 \log D = 1/2 \log a_2'/d + 1/2 \log D \quad (9)$$



**FIGURE 4.** Theoretical impedance plots for  $D = 0.1$  as a function of coating thickness  $d = 1000 \mu\text{m}$  (curve 1),  $100 \mu\text{m}$  (2), and  $10 \mu\text{m}$  (3).

$$\log \Phi_{\min} = a_3 + b_3 \log D = 1/2 \log a_3/d - 1/2 \log D \quad (10)$$

Using certain simplifying assumptions, it can be shown that

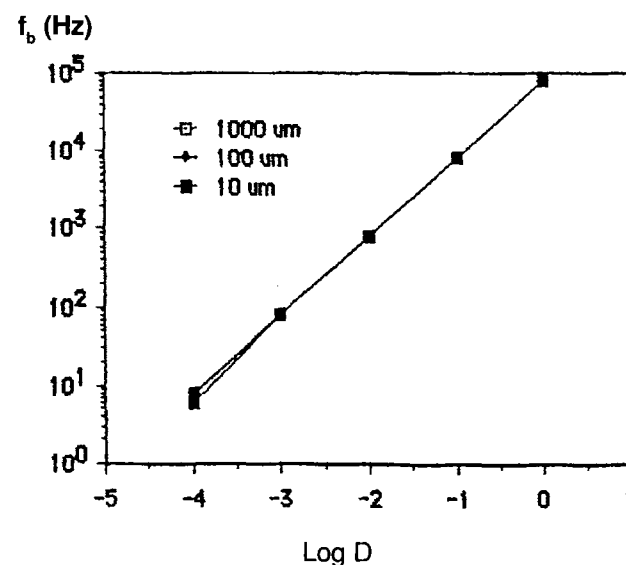
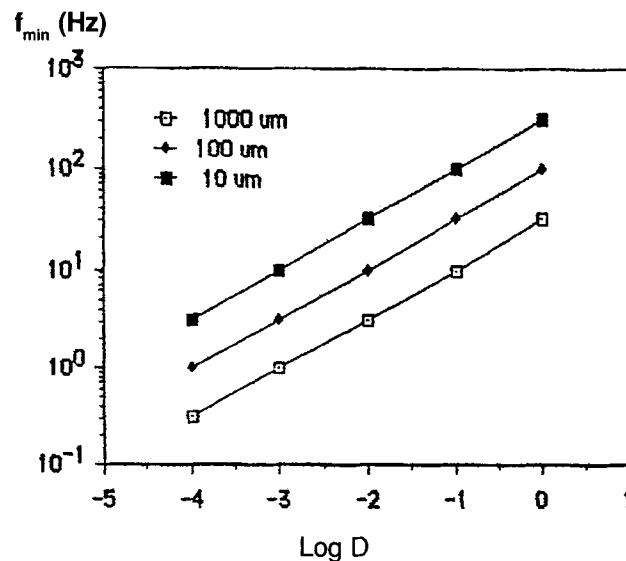
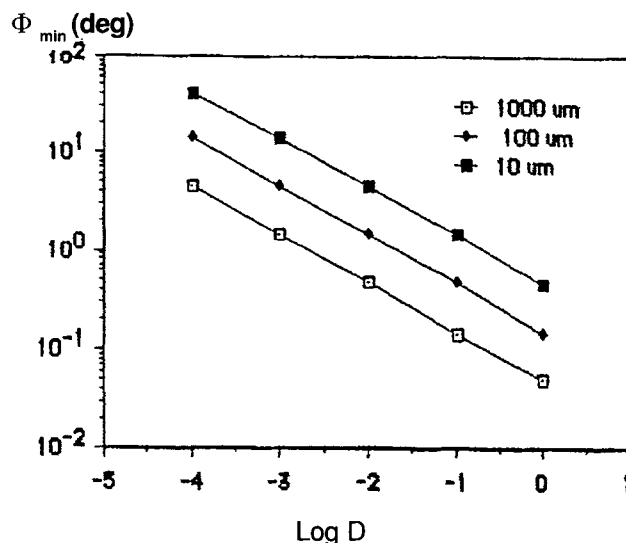
$$f_{\min} = (1/4 \pi^2 C_c C_{dl} R_{po}^2)^{1/2} = (D/4\pi^2 \epsilon \epsilon_0 C_{dl} \rho^2 d)^{1/2} = a_2 (D/d)^{1/2} \quad (11)$$

and

$$\tan \Phi_{\min} = (4 C_c / C_{dl})^{1/2} = (4 \epsilon \epsilon_0 / C_{dl} d D)^{1/2} = a_3 (dD)^{-1/2} \quad (12)$$

According to Equations (11) and (12),  $f_{\min}$  depends on  $(D/d)^{1/2}$ , and  $\tan \Phi_{\min}$  depends on  $(dD)^{-1/2}$ . At constant coating thickness,  $\Phi_{\min}$  becomes smaller, and  $f_{\min}$  moves to higher frequencies with increasing delamination (Figure 5). As discussed above,  $a_2$  and  $a_3$  are expected to change as the coating picks up water and conductive paths develop. In particular, it should be noted that there is a linear relationship between  $f_{\min}$  and  $\rho$  while  $\Phi_{\min}$  is independent of  $\rho$ . A more detailed discussion of the effects of increasing coating conductivity, which is neglected in Haruyama's approach, will be given in Part II of this paper.<sup>9</sup>

The differences between the values of  $f_b$ ,  $f_{\min}$ , and  $\Phi_{\min}$  calculated from the approximations given here (Equations [6], [11], and [12]) and the exact values (data of Figure 3) are less than 5 percent for  $D = 10^{-4}$  and even less for higher values of  $D$ .



**FIGURE 5.** Relationships between  $\Phi_{\min}$ ,  $f_{\min}$ ,  $f_b$ , and  $D$  for three coating thicknesses.

### DELAMINATION OF A POLYBUTADIENE COATING ON STEEL

The experimental data shown in Figure 2 can be interpreted in terms of coating delamination using the approach discussed above.<sup>1-4</sup> Assuming that the value of  $R_{po}(0)$  at time  $t = 0$  is the same for all samples in Figure 2 ( $R_{po}(0) = 7 \times 10^5 \text{ ohm}$ ) and that  $D = 10^{-4}$  at  $t = 0$  ( $R_{po}^0 = 1.4 \times 10^3 \text{ ohm}\cdot\text{cm}^2$ ), one obtains the time dependence of the delamination ratio  $D$  (Figure 6), based on Equation (1) and the definition of  $D$ . Pre-treatments such as passivation in conc.  $\text{HNO}_3$  cause rapid delamination to values of  $D$  close to one in seven days. Initially, delamination proceeds quite

rapidly and then levels off. Using the value of  $R_{po}^0 = 1.4 \times 10^3 \text{ ohm}\cdot\text{cm}^2$  calculated above for a coating thickness  $d = 10 \mu\text{m}^{1-4}$  leads to  $\rho = 1.4 \times 10^6 \text{ ohm}\cdot\text{cm}$  at  $t = 0$  for the specific resistance of the polybutadiene coating (Equation [2]) used in the experiments of Kendig and Mansfeld.<sup>1-4</sup> In the following, it is assumed that  $\rho$  remains constant throughout the exposure test. The more complicated case of increasing delamination and decreasing coating resistance will be treated in Part II of this paper.<sup>9</sup>

Another result obtained by Kendig and Mansfeld<sup>1-4</sup> for polybutadiene coatings on steel is shown in Figure 7 where the time dependence of  $R_{po}$  is compared with that of the delaminated area  $\text{DEL}$

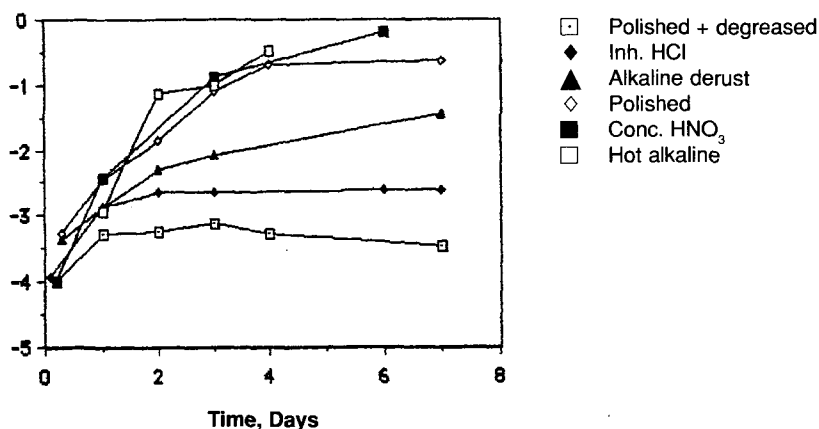


FIGURE 6. Time dependence of delamination ratio  $D$  for the data in Figure 2.

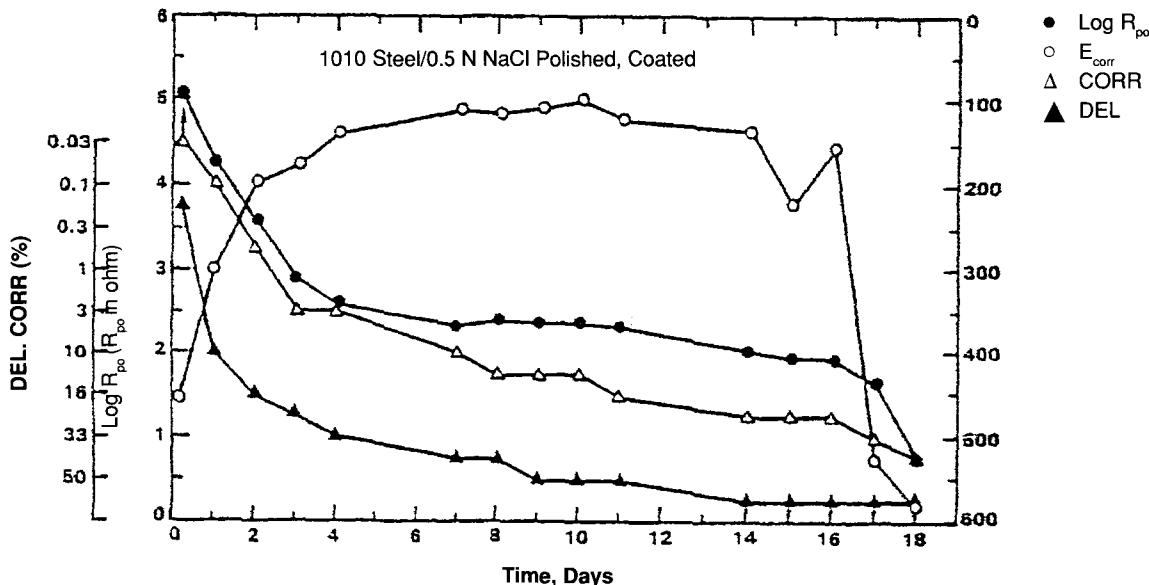
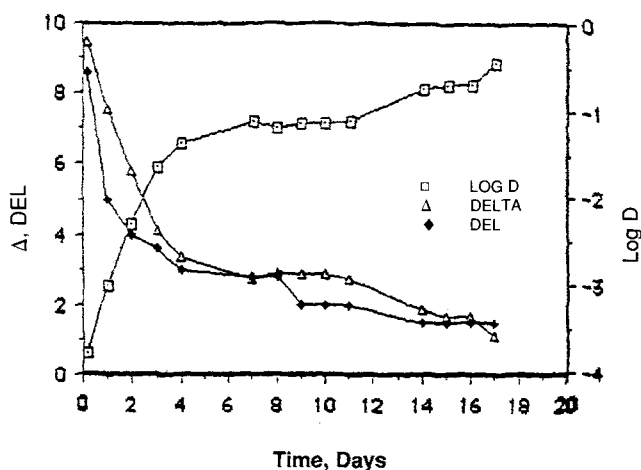


FIGURE 7. Time dependence of  $R_{po}$ , the corroded area  $\text{CORR}$ , the delaminated area  $\text{DEL}$ , and the corrosion potential  $E_{corr}$  for polybutadiene on 1010 steel (polished) during exposure to 0.5 N NaCl ( $A=20 \text{ cm}^2$ ).<sup>2</sup>

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**FIGURE 8.** Time dependence of log  $D$ , the delamination function  $\Delta$ , and DEL (data from Figure 7).

and the corroded area CORR as determined visually according to ASTM D 610. A strong correlation between  $R_{po}$ , CORR, and DEL is evident. In Figure 8, the values of DEL from Figure 7 and  $D$  as calculated from the experimental values of  $R_{po}$  in Figure 7 (Equations [1] and [6], assuming  $R_{po}(0) = 2 \cdot 10^5$  ohm and  $D = 10^{-4}$  for  $t = 0$ ) are plotted vs time and compared to the delamination function  $\Delta$  which is defined as:

$$\Delta = -2.5 \log D \quad (13)$$

This function has values of  $\Delta = 0$  for  $D = 1$  and  $\Delta = 10$  for  $D = 10^{-4}$ , which is probably the lowest value of coating delamination that can be detected experimentally. As a result of this definition,  $\Delta$  will have experimental values between 0 (worst) and 10 (best); therefore, it is the electrochemical equivalent of DEL, which is determined visually as defined in ASTM D 610. The excellent agreement between DEL and  $\Delta$  over the entire test period (Figure 8) suggests that  $R_{po}$  is indeed strongly related to coating delamination.

## CONCLUSIONS

The excellent agreement between the estimate for the degree of delamination based on the experimental values of  $R_{po}$  in Figure 2 and the visually determined data suggests that it is possible to determine the delaminated or corroded area from impedance data. The delamination function  $\Delta$  is the electrochemical equivalent of the value DEL determined according to ASTM D 610. Additional parameters obtained from the impedance spectra

such as the breakpoint frequency  $f_b$ , the minimum of the phase angle  $\Phi_{min}$  and its frequency  $f_{min}$  can be used to follow the degree of delamination and the growth of the corroding area with exposure time, as discussed in Part II of this paper for marine coatings on steel.<sup>9</sup>

In order to calculate the numerical values of the delaminated and corroding area  $A_o$  or the delamination ratio  $D = A_o/A$  from the measured impedance data  $f_b$ ,  $f_{min}$ , or  $\Phi_{min}$ , one needs to know the coating parameters  $\epsilon$  and  $\rho$  and their dependence on exposure time (Equations [6], [7], [11], and [12]). If these data and their changes with exposure time are not available, an estimate of  $A_o$  or  $D$  can be obtained by assuming a constant value of  $C_{dl}^o$  (independent of exposure time) and calculating  $A_o$  or  $D$  from the experimental values of  $C_{dl}$  (Equation [4]).<sup>7,8</sup> This approach becomes difficult in the initial phase of exposure and for thicker coatings (Figures 3[b] and [c]), where  $C_{dl}$  often cannot be extracted from the experimental impedance spectra with sufficient accuracy. In this paper, a very small value of  $D$  has been assumed to be associated with the experimental value  $R_{po}(0)$  for  $t = 0$  (Equation [1]).

The concepts discussed here are being evaluated further in terms of applications in field studies and determination of the remaining corrosion protection by an exposed polymer coating. Various possibilities for the design of instrumentation for such field studies will be assessed based on these concepts.<sup>9</sup>

## ACKNOWLEDGMENT

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