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The Variation of Corrosion Potential With Time for Coated Metal Surfaces

Merlin D. Danford and Ward W. Knockemus



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Merlin D. Danford

George C. Marshall Space Flight Center Marshall Space Flight Center, Alabama

Ward W. Knockemus

Huntington College Montgomery, Alabama



Scientific and Technical Information Branch

## **ACKNOWLEDGMENTS**

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#### TECHNICAL PAPER

# THE VARIATION OF CORROSION POTENTIAL WITH TIME FOR COATED METAL SURFACES

#### INTRODUCTION

The measurement of corrosion potentials ( $E_{\rm CORR}$ ) as determined using the EG&G-PARC model 350A Corrosion Measurement Console are being explored and developed. The purpose is to rank and select materials and coatings for use in seawater/salt air environments such as those experienced by the solid rocket booster cases of the Space Shuttle.

The variation of corrosion rates, electrical resistances, and polarization resistances, as determined by electrochemical methods, with time have been reported earlier [1]. These results were obtained in a study of the behavior of primer-coated 2219-T87 aluminum. Although brief mention of the variation of corrosion potential with time was made, no detailed study of this problem was undertaken. In the present work, a study of the corrosion potentials for coated 4130 steel and primer coated 2219-T87 aluminum has been carried out. The coated steel samples were included to provide a comparison with the work of Wormwell and Brasher [2], who investigated the effects of surface preparation and the type and number of coats of paint on the potential of coated steel specimens immersed in synthetic seawater. Their work extended over a much longer time period (about 5 months), and the measured potentials represented the average for a large number of measurements. The objective of the present work was to make the measurements over a much shorter period of time (about 1 month), and to use only a single sample rather than the average for a large number of samples. However, considerable scatter of the observed data, particularly where the corrosion potentials were recorded manually, make it necessary to develop a computer program to smooth the data before proper interpretation could be made. Details of this program are described in the next section, and a complete listing of the FORTRAN-77 Program is included in the appendix.

## THE SMOOTHING PROGRAM

The basis for the data smoothing procedure has been described by Lanczos [3], and involves smoothing in the large by Fourier analysis. The entire set of data is treated as one unified whole. The routine serves as a low pass filter, in which the true course of the function and superimposed noise are separated. This method of smoothing has the advantage that it is more independent of any special assumptions concerning the nature of the unknown f(x). Only essential details of the method will be given here, and the reader is referred to the original report for further information.

A large number of observations at the points

$$x = 0, h, 2h, ..., nh = 0$$
 (1)

is to be considered. If a properly chosen  $\alpha+\beta x$  is subtracted from f(x),

$$g(x) = f(x) - (\alpha + \beta x) \tag{2}$$

where  $\alpha$  and  $\beta$  are determined by the boundary conditions,

$$g(0) = 0, g(\ell) = 0$$
 (3)

and

$$g(-x) = -g(x) \tag{4}$$

the result is a function which, if made periodic with the period  $2\ell$ , has no discontinuity in either function or derivative. The function g(x) is developed into a pure sine series of the form:

$$g(x) = b_1 \sin \frac{\pi}{Q} x + b_2 \sin \frac{2\pi}{Q} x + \dots$$
 (5)

Since

$$y_k = f(kh), \quad (k = 0, 1, 2, ..., n)$$
 (6)

f(x) is modified to

$$g(x) = f(x) - f(0) - \frac{f(\ell) - f(0)x}{\ell}$$
(7)

and achieves the boundary conditions (3). The coefficients  $b_k$  of the expansion (5) are determined by the condition that at the data points x = kh the series gives the modified basic data g(kh) or the original measurements corrected by  $\alpha+\beta x$ . Thus:

$$b_k = \frac{2}{n} \sum_{\alpha=1}^{n-1} g(\alpha h) \sin k \frac{\alpha \pi}{n}$$
 (8)

In the absence of noise, the Fourier coefficients  $b_1$ ,  $b_2$ , ...,  $b_m$  have certain values, but are practically zero beyond  $b_m$ . Then the Fourier synthesis

$$g(x) = b_1 \sin \frac{\pi}{\ell} x + b_2 \sin \frac{2\pi}{\ell} x + ... + b_m \sin \frac{m\pi}{\ell} x$$
 (9)

properly interpolates the function, not only in the data points but at all points of the range. Thus, all of the high frequency components of the noise are eliminated.

The method of determining the cutoff frequency is different in the present method from that proposed by Lanczos. Terms may be added singly by setting  $k_{max} = -1, -2, ..., -n$ . In this way, it can be determined visually where noise contributions begin to enter. A method for automatic selection of  $k_{max}$  has also been developed in the present computer program, but has been tested for only a few cases. In this method the sum

$$\beta = \frac{1}{\sqrt{n-1}} \left( b_1^2 + b_2^2 + \dots b_n^2 \right)^{1/2}$$
 (9)

is first formed. The functions

G1(m) = 
$$\frac{1}{\sqrt{n-1}} (b_1^2 + b_2^2 + ... + b_m^2)^{1/2}$$
 (10)

are formed for m = 1, 2, ..., n. The value of  $\beta$  is then subtracted from each of the values of G1(m), resulting in a curve of the type shown by the solid curve in Figure 1. The upper half of this function is fitted to a polynomial of degree 3 by the method of least squares and the differences

$$Y1(m) = G1(m) - Y(m)$$
 (11)

where Y(m) are the values obtained from the cubic equation, are calculated. The quantities

$$A = \frac{Y1(m)}{Y(m)} \text{ exp. } [-bX^2(m)]$$
 (12)

are examined beginning at m = n and proceeding toward smaller m. In equation (12),

$$b = 2.303/X_{max}^{2}$$
 (13)

Equation (13) was obtained by setting  $\exp(-bX_{max}^2) = 0.1$ . The exponential factor in equation (12) is included to damp some possibly large values of A at large m due to small values of Y(m). When A exceeds a certain value, in this case set at 0.6, the value of  $k_m$  for the truncated series is set at

$$k_{\text{max}} = n - m + 2 \tag{14}$$

where n is the total number of coefficients and m is the number of values of A which have been examined. The value of 0.6 may require some adjustment as further cases are examined. The original function with the noise removed is obtained by reconstituting the data series with the number of terms given by  $k_m$  included. There is some flexibility in choosing the value of A and the extra quantity of 2 terms in equation (13), since there is a range of terms for which the smoothed function changes very little (shown in Figure 2 for a coated 4130 steel sample).

#### **EXPERIMENTAL**

Measurements of corrosion potentials ( $E_{\rm CORR}$ ), corrosion rates (obtained with the polarization resistance method) and electrical resistance were made over a period of 45 days for a 4130 steel sample coated with Braycote 137 preservative compound (Sample 1) and for a period of 32 days (Sample 2). The sample holder employed is shown in Figure 3. The metal specimens were 1.43 cm (9/16 in.) in diameter and 0.137 cm thick. The metal samples were smoothed by wet sanding with 220A silicon carbide paper and sprayed on one side with a 20 percent by weight solution of Braycote 137 in 1,1,1-trichloroethane to a thickness of 0.005 cm (0.002 in.), as measured with a wet thickness gauge.

Aluminum samples (2219-T87) were prepared by a 15 min immersion in hot alkaline cleaner, followed by a 15 min suspension in "Smut-Go" chromate deoxidizer. The samples were then treated with Alodine 1200 (conversion coat) for a period of 2 min and sprayed on one side to a measured thickness with TT-P-1757 zinc chromate primer. The samples were placed in the sample holder, with an area of 1.0 cm<sup>2</sup> exposed, and immersed in a test solution consisting of 3.5 percent NaCl buffered at pH 5.5 for the entire test period.

Data for electrical resistance were obtained with the EG&G-PARC Model 356 IR Compensation Module in conjunction with the EG&G-PARC Model 350A Corrosion Measurement Console. Data were collected daily for the first few days for each sample, after which the frequency of data collection was decreased. Values of  $E_{\rm CORR}$  and corrosion current ( $I_{\rm CORR}$ ) were obtained using the polarization resistance method where possible, with data being taken on alternate days. The small currents involved in the study of coated surfaces disturb the sample surfaces very little, so that repeated measurements can be made.

The EG&G-PARC Model 350A Corrosion Measurement Console was used for collection of polarization resistance data at 25°C. Data were collected at 0.5 mV intervals at a scan rate of 0.1 mV/sec. The measurement range for all determinations was -20 to +20 mV with respect to  $E_{CORR}$ , with all data being corrected for IR-drop. The data were stored on disk and transferred to a computer for calculation of the polarization resistance ( $R_p$ ),  $E_{CORR}$ , anodic and cathodic Tafel constants and  $I_{CORR}$  using the program POLCURR [4].

#### **RESULTS AND DISCUSSION**

#### A. Braycote 137 Preservative

The variation of  $E_{\rm CORR}$  with time for Braycote 137 coated sample 2 is shown in Figure 4. In this case, the experimental values of  $E_{\rm CORR}$ , shown at the left side of Figure 4, were obtained through least squares refinement of the experimental data by the polarization resistance method using POLCURR. The smoothed data are shown at the right. In this case, three terms in the truncated series, as chosen by the automatic selection technique, were required for the smoothed data. A peak occurs at about 20 days of the exposure period. This is almost exactly the same period for the peak occurrence as obtained by Wormwell and Brasher [2] (Fig. 5) for paint-coated steel samples, although their data were the average for a large number of samples. The present data are the result of a single measurement for each time interval. The variations of corrosion rate and electrical resistance for the same sample are shown in Figure 6. A peak in the resistance-time curve occurs at 15 days, while the corrosion rate-time curve begins to increase after about 20 days. The  $E_{\rm CORR}$ -time curve thus correlates rather well with the curves of Figure 6.

The  $E_{\rm CORR}$ -time curves for Braycote 137 sample 1 are shown in Figure 7, with the observed values on the left and the smoothed values on the right. In this case, no measurable corrosion current was observed until after 27 days, which precluded the use of POLCURR. The measurements were, therefore, made manually and resulted in a great deal of data scatter. The smoothed curve at the right contained four terms in the truncated series using the automatic selection method. The first peak at 7 days is not considered significant, and the major peak of the curve occurs at about 31 days. A peak occurs at 24 days in the resistance-time curve (Fig. 8), while the corrosion rate becomes measurable at about 27 days. The maximum for the smoothed  $E_{\rm CORR}$ -time curve therefore correlates well with the curves of Figure 8.

#### B. Primer Coated Aluminum

The  $E_{\rm CORR}$ -time curves for primer coated 2219-T87 aluminum are shown in Figure 9. The measurements were carried out over a period of 30 days, during which the curves showed no significant variation. This is in contrast to observations for the coated steel samples in the present work, as well as the results of Wormwell and Brasher [2]. However, the resistance-time curves and corrosion rate-time curves (Fig. 10) for the two samples show a great deal of activity, with a sharp drop in resistance after only a few days and a peak in the corrosion rate-time curves at about 16 days. It appears, therefore, that  $E_{\rm CORR}$  measurements cannot be used in the case of aluminum to evaluate corrosion behavior unless, possibly, the measurements are extended over a much longer time period.

#### CONCLUSIONS

It is clear from these results that there are important differences in the behavior of coated aluminum and steel as far as electrochemical measurements are concerned. The  $E_{\rm CORR}$ -time curves for Braycote 137 coated steel show a maximum after a period of several days, the positions of which correlate well with observations for resistance-time curves and corrosion rate-time curves. Also, since there is considerable scatter in the data, a smoothing procedure must be used before proper interpretation of the data can be accomplished when measurements are made with a single sample. On the other hand, the  $E_{\rm CORR}$ -time curves for primer coated aluminum show no significant variations with time over a 30 day period, although considerable activity is indicated in the resistance-time and corrosion rate-time curves.

#### **REFERENCES**

- 1. Danford, M. D. and Higgins, R. H.: An Electrochemical Study of the Corrosion Behavior of Primer Coated 2219-T87 Aluminum. NASA Technical Paper 2459, April 1985.
- 2. Wormwell, F. and Brasher, D. M.: J. Iron Steel Inst., Vol. 162, 1949, p. 129.
- 3. Lanczos, C.: Applied Analysis, Prentice Hall, Inc., 1961, p. 331-338.
- 4. Gerchakov, S. M., Udey, L. R., and Mansfeld, F.: An Improved Method for Analysis of Polarization Resistance Data. Corrosion, Vol. 37, 1981, p. 696.

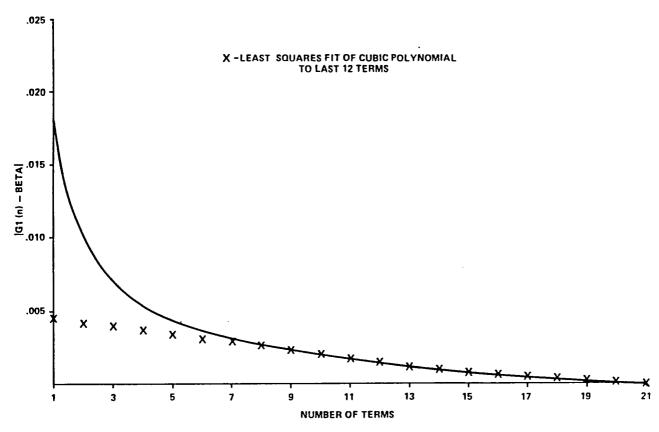


Figure 1. Variation of |G(n)-BETA| with the number of terms in truncated series.

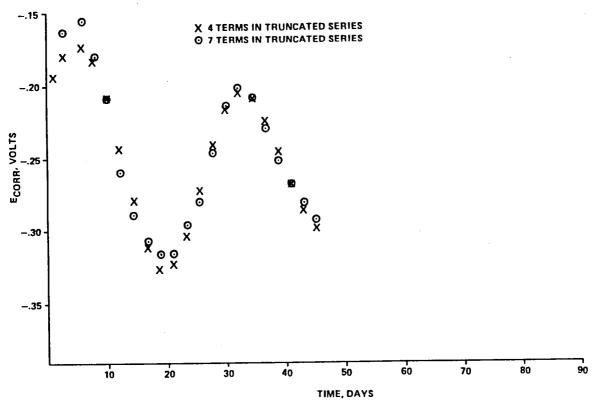


Figure 2.  $E_{\mbox{CORR}}$  versus time with 4 and 7 terms in truncated series.

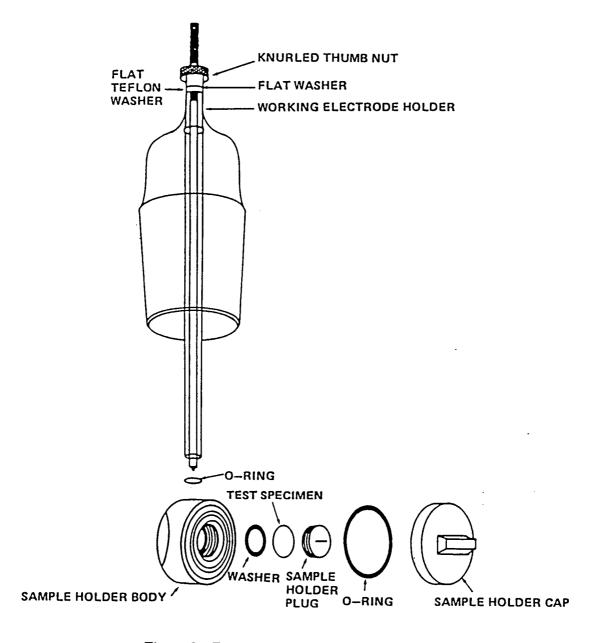


Figure 3. Exploded view of the sample holder.

# **ORIGINAL DATA**

# SMOOTHED DATA 3 TERMS IN TRUNCATED SERIES AUTOMATIC SELECTION

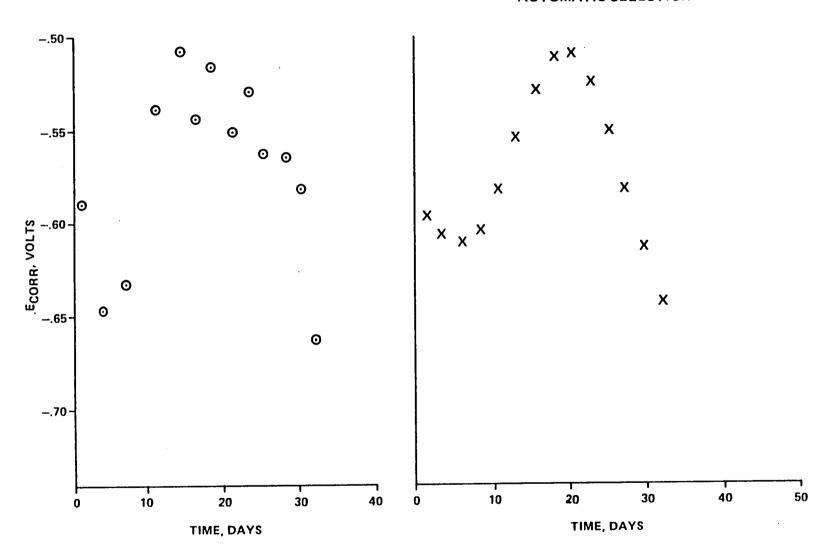


Figure 4. Raw E<sub>CORR</sub> versis time (left) and smoothed data versus time (right) for Braycote Sample 2.

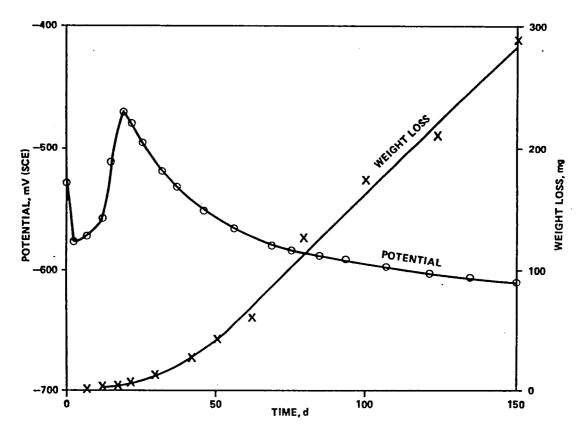


Figure 5. Potential-time and weight loss curves for painted steel from Wormwell and Brasher.

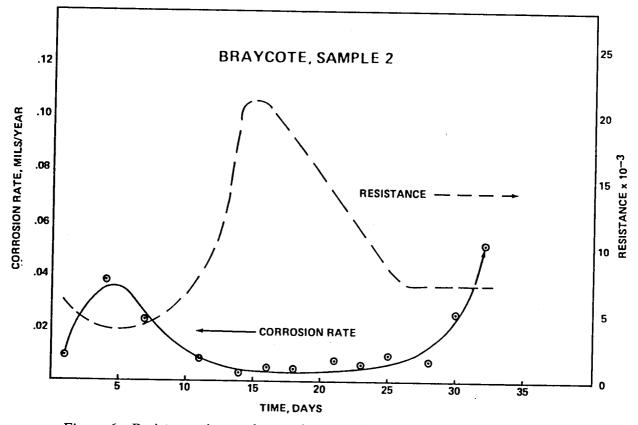


Figure 6. Resistance-time and corrosion rate-time curves for Braycote Sample 2.

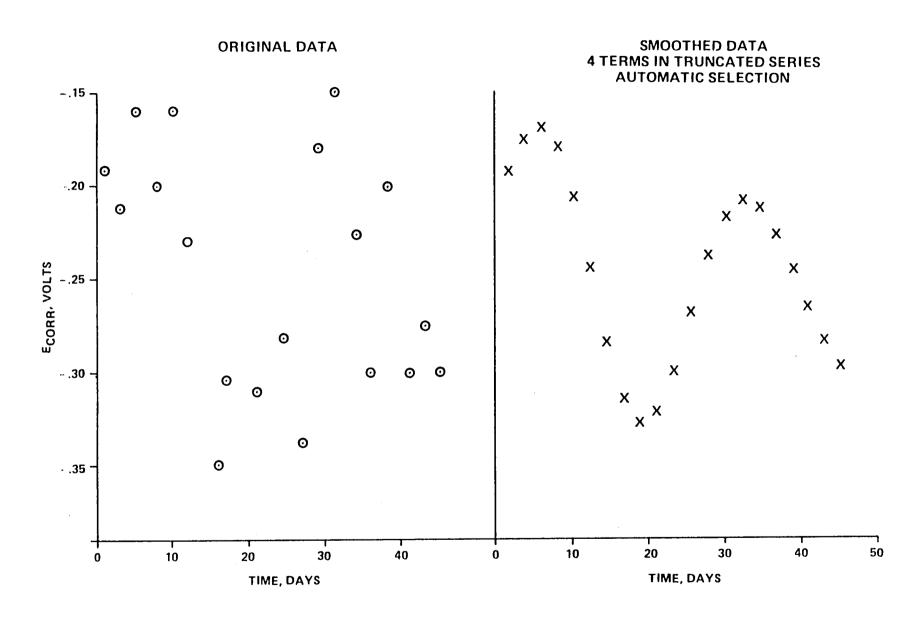


Figure 7. Raw E<sub>CORR</sub> versus time (left) and smoothed data versus time (right) for Braycote Sample 1.

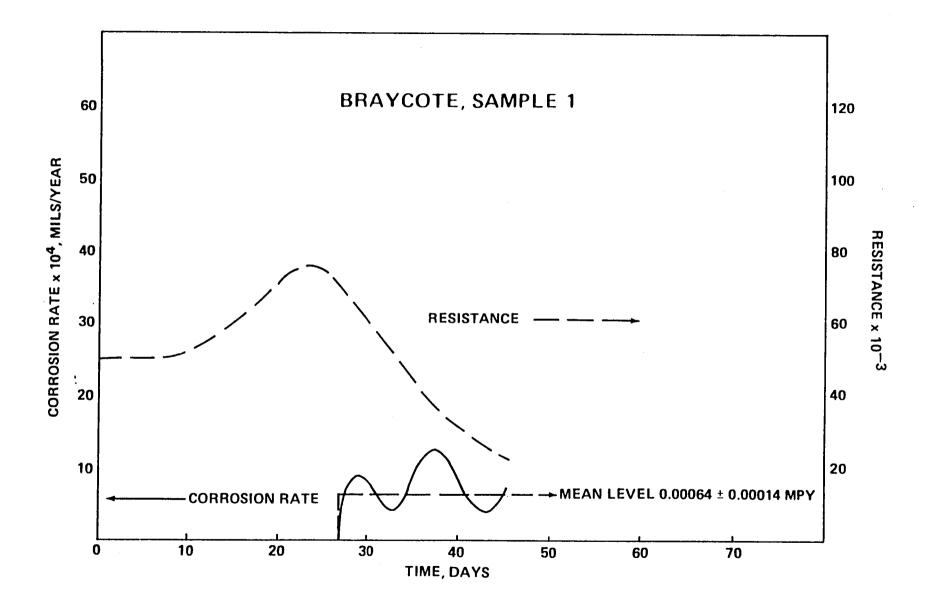


Figure 8. Resistance-time and corrosion rate-time curves for Braycote Sample 1.

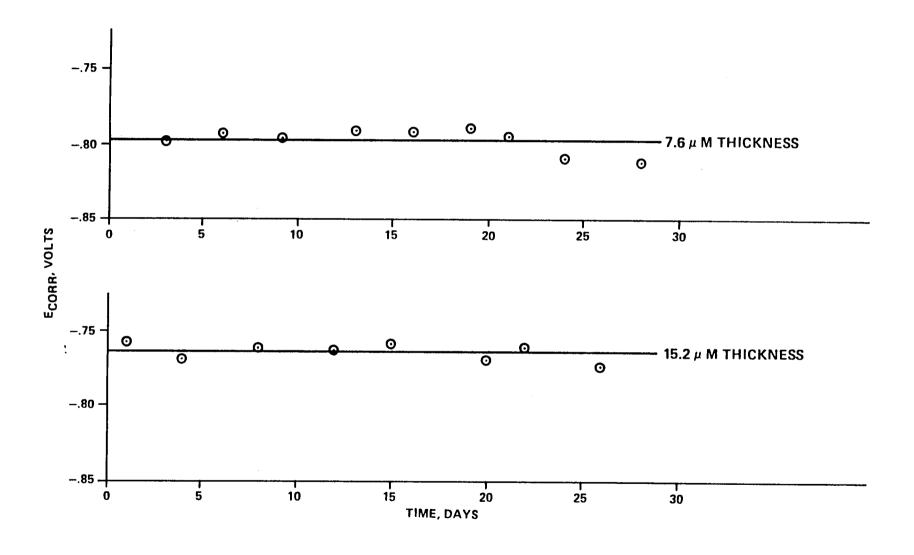


Figure 9.  $E_{\mbox{CORR}}$  versus time for primer coated 2219-T87 aluminum.

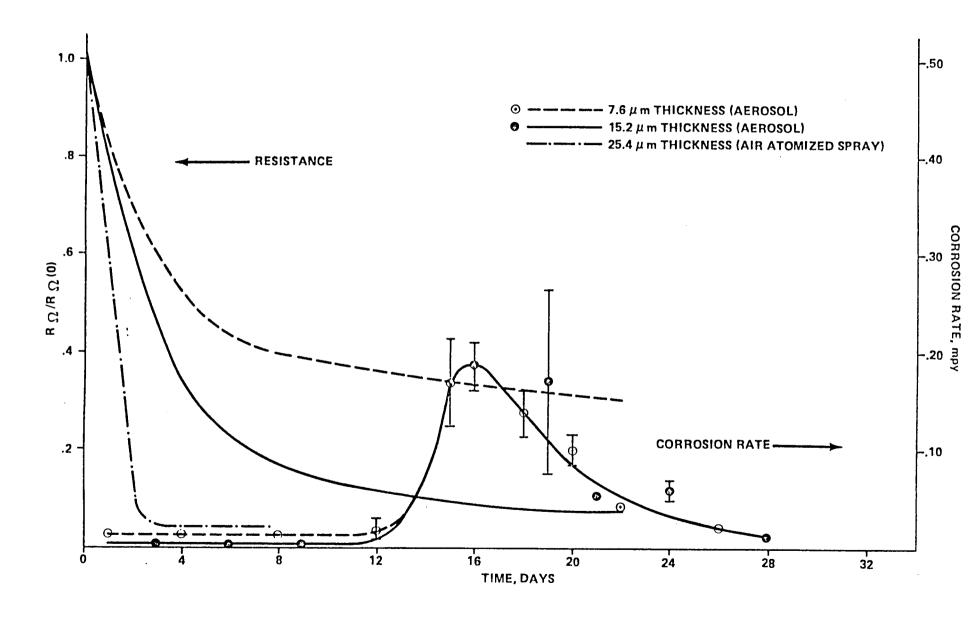


Figure 10. Normalized resistance-time and corrosion rate-time curves for TT-P-1757 primers.

#### **APPENDIX**

Listing of the Fortran-77 program used for smoothing the E<sub>CORR</sub>-time data.

```
PROGRAM main
        ANALYSIS OF FIRST ORDER DIFFERENCE RESULTS
        ORIGINAL DATA MUST BE EQUALLY SPACED. IF THEY ARE NOT, THE
        APPROPRIATE QUESTION IN THE DATA INPUT MUST BE ANSWERED NO.
        THE INCLUDED LAGRANGIAN INTERPOLATING ROUTINE WILL PROVIDE
C
        EQUAL SPACING WITH THE ADDITION OF ONE DATA POINT.
        KMAX IS DEFINED IN SUBROUTINE LOPAS. THE NUMBER OF
        COEFFICIENTS IN THE TRUNCATED SERIES CAN BE CHOSEN AT WILL
        BY SETTING KMAX EQUAL TO -1,-2,...,-NPTS.
                                                     AUTOMATIC
        DETERMINATION OF THE NUMBER OF COEFFICIENTS IN THE TRUNCATED SERIES IS CARRIED OUT BY A LEAST SQUARES
        FITTING PROCEDURE IF KMAX IS ENTERED AS 1.
                                                       THIS METHOD
        HAS NOT YET BEEN THOROUGHLY TESTED.
        IMPLICIT REAL*8(A-H,O-Z)
        CHARACTER*3 AB, AC
        CHARACTER*10 IFILEN
        DIMENSION TITLE(18),X(100),Y(100)
        DIMENSION TX(201), TY(201), AUX(201)
        COMMON TX, TY, AUX
C
        SET UP PROBLEM AND INPUT DATA
C
        WRITE(6,15)
        FORMAT(/,1X,'READ TITLE',/)
 15
         READ(5,5) TITLE
 5
         FORMAT(18A4)
         WRITE(6,25)
         FORMAT(/,1X,'READ LOWER VALUE OF X FOR SMOOTHING',/)
 25
         READ(5,20) SL
         WRITE(6,30)
         FORMAT(/,1X,'READ UPPER VALUE OF X FOR SMOOTHING',/)
 30
         READ(5,20) SU
         WRITE(6,75)
         FORMAT(/,1X,'READ KMAX',/)
 75
         READ(5,125) KMAX
 125
         FORMAT(13)
 20
         FORMAT(F10.0)
         FORMAT(1X, F8.4, 1X, F9.5)
 200
         WRITE(6,310)
         FORMAT(/,1X,'SAVE SMOOTHED DATA?(YES)(NO)',/)
  310
         FORMAT(A3)
  320
         READ(5,320) AB
         IF(AB.EQ.'YES') THEN
         WRITE(6,215)
         FORMAT(/,1X,'READ FILENAME FOR SMOOTHED DATA',/)
  215
         READ(5,220) IFILEN
         END IF
  220
         FORMAT (A10)
         WRITE(6,330)
         FORMAT(/,1X,'ARE DATA EQUALLY SPACED?(YES)(NO)',/)
  330
         READ(5,320) AC
 C
                                            READ ISENT, X, Y: E.G.
         READ OBSERVED DATA TO SENTINEL.
 C
         0,1.0,.235 CARRIAGE RETURN. CONTINUE FOR ALL DATA POINTS.
         AFTER ALL DATA HAVE BEEN ENTERED, ENTER 1,0,0 CARRIAGE RETURN.
         WRITE(6,35)
         FORMAT(/,1X,'READ DATA TO SENTINEL',/)
  35
```

```
NX=1
 40
         READ(5,*) ISENT, X(NX), Y(NX)
         IF(ISENT.EQ.1) GO TO 45
         NX=NX+1
         GO TO 40
 45
         NX=NX-1
        NPTS=NX
C
C
        CARRY OUT INTERPOLATION IF DATA POINTS ARE NOT EQUALLY SPACED
C
         IF(AC.EQ.'NO') THEN
         DEL=(X(NX)-X(1))/FLOAT(NX)
        NPTS=NX+1
        DO 90 I=1,NPTS
        K=I-1
         TX(I)=FLOAT(K)*DEL+X(1)
 90 _
         TY(I)=YLAG(TX(I),X,Y,0,3,NX,IEX)
        GO TO 340
        END IF
        DO 345 I=1,NPTS
        TX(I)=X(I)
 345
         TY(I)=Y(I)
 340
        OPEN(4, FILE='PRN.LST')
        WRITE(4,50) TITLE
        FORMAT(1X, 18A4, /)
 50
        CALL LOPAS(SL, SU, NPTS, KMAX)
        DO 300 K=1,NPTS
        TY2=TY(K)-AUX(K)
 300
        AUX(K)=TY2
C
C
        OUTPUT ORIGINAL AND SMOOTHED DATA
C
        WRITE(4,55)
 115
 55
        FORMAT(/,7X,'ORIGINAL DATA',/)
        WRITE(4,60)
 60
        FORMAT(5X,'X',14X,'Y',/)
        WRITE(4,65)(X(K),Y(K),K=1,NX)
 65
        FORMAT(E11.5,3X,E11.5)
        WRITE(4,70)
        FORMAT(/,7X,'SMOOTHED DATA',/)
 70
        WRITE(4,60)
        WRITE(4,65)(TX(K),AUX(K),K=1,NPTS)
        CLOSE (-4)
        IF(AB.EQ.'YES') THEN
        OPEN(2, FILE=IFILEN, STATUS='NEW')
        WRITE(2,200)(TX(I),AUX(I),I=1,NPTS)
        CLOSE(2,STATUS='KEEP')
        END IF
        END
C
        FUNCTION YLAG(XI,X,Y,IND1,N1,IMAX,IEX)
        IMPLICIT REAL*8(A-H,O-Z)
C
C
        LAGRANGIAN INTERPOLATION
C
        DIMENSION X(1), Y(1)
С
        IND=IND1
        N=N1
        IEX=0
```

```
IF(N.LE.IMAX) GO TO 10
        N=IMAX
        IEX=N
        IF(IND.GT.O) GO TO 40
 10
        DO 20 J=1,IMAX
        IF(XI-X(J)) 30,45,20
        CONTINUE
 20
        IEX=1
        GO TO 70
 30
        IND=J
 40
        IF(IND.GT.1) GO TO 50
        IEX=-1
 50
        INL=IND-(N+1)/2
        IF(INL.GT.O) GO TO 60
        INL=1
        INU=INL+N-1
 60
        IF(INU.LE.IMAX) GO TO 80
 70
        INL=IMAX-N+1
        INU=IMAX
        S=0.0
 80
        P=1.0
        DO 25 J=INL, INU
        P=P*(XI-X(J))
        D=1.0
        DO 15 I=INL, INU
        IF(I.NE.J) GO TO 90
        XD=XI
        GO TO 15
 90
        XD=X(J)
 15
        D=D*(XD-X(I))
        S=S+Y(J)/D
 25
        YLAG=S*P
 35
        RETURN
 45
        YLAG=Y(J)
        GO TO 35
        END
C
        SUBROUTINE LOPAS(SL,SU,NS,KMAX)
C
        REMOVES NOISE FROM DATA SET, S, DI BY SMOOTHING IN THE LARGE
C
C
        LANCZOS, APPLIED ANALYSIS(1956), P.331-338
C
C
        S
                   X-array
Č
        DI
                   Y-array to be smoothed
C
        NS
                   Number of X,Y points
00000
        BY
                   Noise determined by LOPAS
        COEF
                   Fourier Coefficients
        GX
                   Working array
        KMAX
                   Number of coefficients in truncated series
                   >0: KMAX to be found by LOPAS
C
                   <0: KMAX=IABS(KMAX) read in
                   No smoothing for values X<X(SL)
        SL
C
        SU
                   No smoothing for values X>X(SU)
C
        IMPLICIT REAL*8(A-H,O-Z)
        DIMENSION GX(257), V(8), Y(201), G1(100), Y1(201)
        DIMENSION S(201), DI(201), BY(201), COEF(512)
        COMMON S, DI, BY
        DATA ZRO, TWO, PI/0.0D0, 2.0D0, 3.141592654D0/
C
```

```
IF((SU.LT.SL).OR.(NS.GT.257)) GO TO 100
 C
 C
          EXPAND DATA INTO FOURIER SERIES
 C
          PS=PI/FLOAT(NS)
          SLP=(DI(NS)-DI(1))/(S(NS)-S(1))
         NN=NS-1
         GX(NS) = ZRO
         GX(1) = ZRO
         COEF(1)=0
         DO 12 N=2, NN
  12
         GX(N)=DI(N)-DI(1)-S(N)*SLP
         DO 20 K=1,NS
         SUM=ZRO
         DO 15 J=2,NS
  15
         SUM=SUM+GX(J)*DSIN(K*(J-1)*PS)
  20
         COEF(K)=TWO*SUM/FLOAT(NS)
 C
 C
         REMOVE HIGH FREQUENCY TERMS
         SUM=ZRO
         DO 25 J=1,NS
         NJ=NS-J+1
  25
         SUM=SUM+COEF(NJ)**2
         BETA=DSQRT(SUM/FLOAT(NS-1))
         IF(KMAX.LT.O) THEN
         KMAX=IABS(KMAX)
         T=100.0
         GO TO 42
         END IF
         DO 200 I=1,NS
         NI=NS-I+1
         G1(NI)=0.0
         DO 210 J=1,NI
         TERM=COEF(J)**2
 210
         G1(NI)=G1(NI)+TERM
         G1(NI)=DSQRT(G1(NI)/FLOAT(NS-1))
 200
         G1(NI)=DABS(G1(NI)-BETA)
         CALL LSTSQR(NS,S,G1,T,V)
        DO 305 I=1,NS
        NI=NS-I+1
        Y(NI)=V(1)+V(2)*(S(NS)-S(NI))+V(3)*(S(NS)-S(NI))**2+V(4)*
         (S(NS)-S(NI))**3
305
        Y1(NI)=G1(NI)-Y(NI)
        B=2.302585/S(NS)**2
        DO 310 I=1,NS
        NI=NS-I+1
        IF(Y(NI).EQ.0.0) GO TO 310
        A=Y1(NI)/Y(NI)*DEXP(-1.0*B*S(NI)**2)
        IF(A.GT.0.60) THEN
        KMAX=NI+1
        GO TO 42
        END IF
 310
        CONTINUE
C
C
        RECONSTITUTE DATA SERIES
C
 42
        DO 50 J=1,NS
        SUM=ZRO
        DO 45 K=1,KMAX
```

```
45
        SUM=SUM+COEF(K)*DSIN(K*(J-1)*PS)
        BY(J)=SUM+DI(1)+SLP*S(J)
 50
C
        WRITE(4,5000) BETA, NS, KMAX, SL, SU
        DO 60 K=1.NS
        IF((S(K).LT.SL).OR.(S(K).GT.SU)) THEN
        BY(K)=0.0
        GO TO 60
        END IF
        BY(K)=DI(K)-BY(K)
 60
        CONTINUE
C
        FORMAT(/,1X,'LOPAS CALLED',/,1X,'BETA = ',E11.5,/,1X,'NCOF = ',I5, ',NTERMS = ',I5,/,1X, 'SL = ',F5.2, '
 5000
     1
          , SU = ', F6.2, /)
     1
C
         WRITE(4,300) T
         FORMAT(/,1X,'PERCENT GOODNESS OF FIT = ',F7.2,/)
 300
         RETURN
C
         WRITE(4,5500)
 100
         DO 70 K=1,NS
 70
         BY(K) = ZRO
         RETURN
         FORMAT(1H ,'LOW PASS DATA WINDOW NOT USED',/)
 5500
         END
C
         SUBROUTINE LSTSQR(NS,S,G1,T,V)
C
         SUBROUTINE FOR FITTING POLYNOMIAL OF DEGREE D
C
C
Ċ
         T=PERCENT GOODNESS OF FIT
C
         HERE, UPPER HALF OF DATA ARE FITTED BY LEAST SQUARES WITH
C
         A POLYNOMIAL WITH DEGREE EQUAL TO 3
C
C
         IMPLICIT REAL*8(A-H,O-Z)
         INTEGER D, D2
         DIMENSION S(201), G1(100), A(8,8), R(8), V(8), P(50), X(100), Y(100)
C
         NA=NS/2
         NP=NS-NA+1
         D=3
         D2=2*D
         N=D+1
         DO 250 I=1,NP
         NI=NS-I+1
         X(I)=S(NS)-S(NI)
 250
         Y(I)=G1(NI)
         DO 15 J=2, D2+1
         P(J) = 0.0
         DO 20 K=1,NP
         P(J)=P(J)+X(K)**(J-1)
 20
         CONTINUE
 15
         P(1)=NP
         R(1)=0.0
         DO 25 J=1,NP
 25
         R(1)=R(1)+Y(J)
         IF(N.EQ.1) GO TO 30
         DO 35 J=2,N
```

```
R(J) = 0.0
       DO 40 K=1,NP
40
       R(J)=R(J)+Y(K)*X(K)**(J-1)
35
       CONTINUE
30
       DO 45 J=1,N
       DO 50 K=1,N
       A(J,K)=P(J+K-1)
50
45
       CONTINUE
       IF(N.EQ.1) THEN
       V(1)=R(1)/A(1,1)
       GO TO 110
       END IF
       DO 55 K=1,N-1
       I=K+1
       L=K
60
       IF((DABS(A(I,K))).GT.(DABS(A(L,K)))) THEN
       L=I
       END IF
       IF(I.LT.N) THEN
       I=I+1
       GO TO 60
       END IF
       IF(L.EQ.K) GO TO 210
       DO 65 J=K,N
       Q=A(K,J)
       A(K,J)=A(L,J)
65
       A(L,J)=Q
       Q=R(K)
       R(K)=R(L)
       R(L)=Q
210
       I=K+1
70
       Q=A(I,K)/A(K,K)
       A(I,K)=0.0
       DO 75 J=K+1,N
75
       A(I,J)=A(I,J)-Q*A(K,J)
       R(I)=R(I)-Q*R(K)
        IF(I.LT.N) THEN
        I=I+1
       GO TO 70
       END IF
        CONTINUE
55
        V(N)=R(N)/A(N,N)
       DO 80 I=N-1,1,-1
        Q=0.0
       DO 85 J=I+1,N
        Q=Q+A(I,J)*V(J)
        V(I) = (R(I) - Q)/A(I,I)
85
        CONTINUE
80
110
        Q = 0.0
        DO 90 J=1,NP
90
        Q=Q+Y(J)
        FM=Q/FLOAT(NP)
        T=0.0
        G=0.0
        DO 95 J=2,NP
        Q = 0.0
        DO 100 K=1,N
        Q=Q+V(K)*X(J)**(K-1)
100
        T=T+(Y(J)-Q)**2
95
        G=G+(Y(J)-FM)**2
```

IF(G.EQ.0.0) THEN
T=100.0
GO TO 105
END IF
T=100.0\*DSQRT(1.0-T/G)
RETURN
END

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The variation of corrosion potential (E <sub>CORR</sub> ) with time has been measured for 4130 steel coated with a preservative compound and for primer coated 2219-T87 aluminum. The data for coated steel samples show a great deal of scatter, and a smoothing procedure has been developed to enable proper interpretation of the data. The E <sub>CORR</sub> -time curves for coated steel exhibit a maximum, in agreement with the results of previous studies, where the data were the average of those for a large number of samples, while the present data were obtained from a single sample. In contrast, the E <sub>CORR</sub> -time curves for primer coated 2219-T87 aluminum samples show no significant variations, although considerable activity is indicated by the resistance-time and corrosion rate-time curves.					
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