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ELECTROCHEMICAL CORROSION STUDIES

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ELECTROCHEMICAL CORROSION STUDIES

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ABSTRACT

Objectives of these investigations are to gain famili-
arity with the Model 350 Corrosion Measurement Console,
to determine if metal protection by grease coatings
can be measured by the polarization-resistance method,
and to compare corrosion rates of 4130 steel coated
with various greases. Results show that grease pro-
tection of steel may be determined electrochemically.
Studies were also conducted to determine the effective-
ness of certain corrosion inhibitors on aluminum and
steel.

ACKNOWLEDGEMENTS

INTRODUCTION

General Theory of Electrochemical Corrosion and Corrosion Rate Measurement

Pure and impure, homogeneous or heterogeneous metallic materials corrode to lower the Gibb's free energy of the system. Corrosion returns the metal to its natural oxidation state, usually an oxide or hydrated oxide. Free, "active" metals (those with negative half-cell potentials in a Table of Standard Reduction Potentials) are in a meta-stable state; they wait only for an oxidant, and sometimes an electrolyte solution to return them to a stable oxidized form.

The electrochemical theory of corrosion rests on the assumption that any metal surface can have areas where metal atoms are oxidizable and other areas where electron acceptor atoms or groups can be reduced. Oxidation (metal dissolution or corrosion) areas are named anodic sites and areas on the metal surface where reduction can occur are named cathodic sites. Figure 1 illustrates this.

The general reactions:
at the anodic sites: $M \longrightarrow M^{n+} + n\ e^-$

at the cathodic sites: $A + n\ e^- \longrightarrow$ Product species

For iron or steel on the atomic level the reactions in an oxygen-water environment might be as shown by Figure 2.

Although there is only one anodic reaction (metal atom oxidation and dissolution), the several possible reactions that might occur on the cathode sites are the following:

1. Hydrogen ion reduction: $2\ H^+ + 2\ e^- = H_2$ (pH less than 5)

2. Oxygen reduction: $O_2 + 4\ H^+ + 4\ e^- = 2\ H_2O$ (low pH)

3. Oxygen reduction: $O_2 + 2\ H_2O + 4\ e^- = 4\ OH^-$ (high pH)

4. Water reduction: $2\ H_2O + 2\ e^- = H_2 + 2\ OH^-$ (neutral, high pH)

5. Metal ion reduction: $Cu^{++} + 2\ e^- = Cu$ (typical)
$$Fe^{+3} + e^- = Fe^{++}$$

6. Oxy-anion reduction: $NO_3^- + e^- + 3\ H^+ = HNO_2 + H_2O$

(low pH)
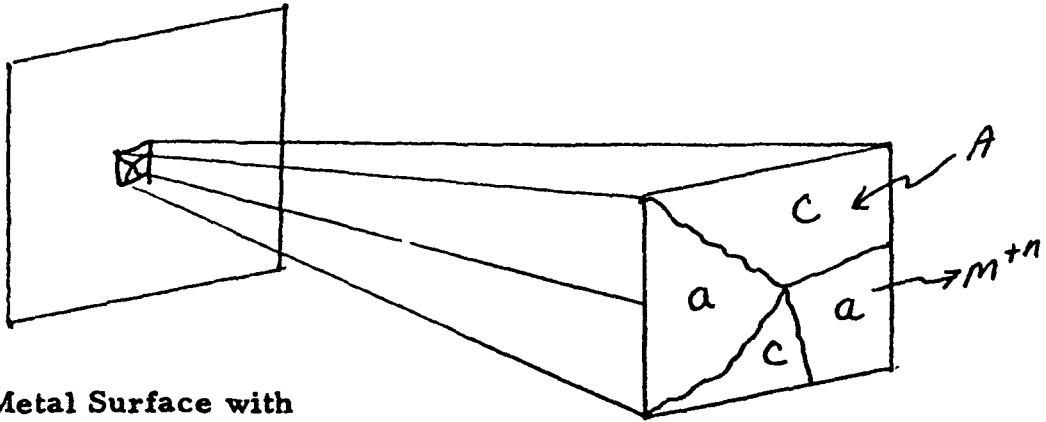
Metal Surface with
Local Corrosion

a = anodic site
c = cathodic site
A = reducible species migrating to cathodic site
M^{+n} = metal ion departing anodic site

Figure 1   Anodic and Cathodic Sites on Metal Surface

c = cathodic site metal atoms
a = anodic site metal atoms
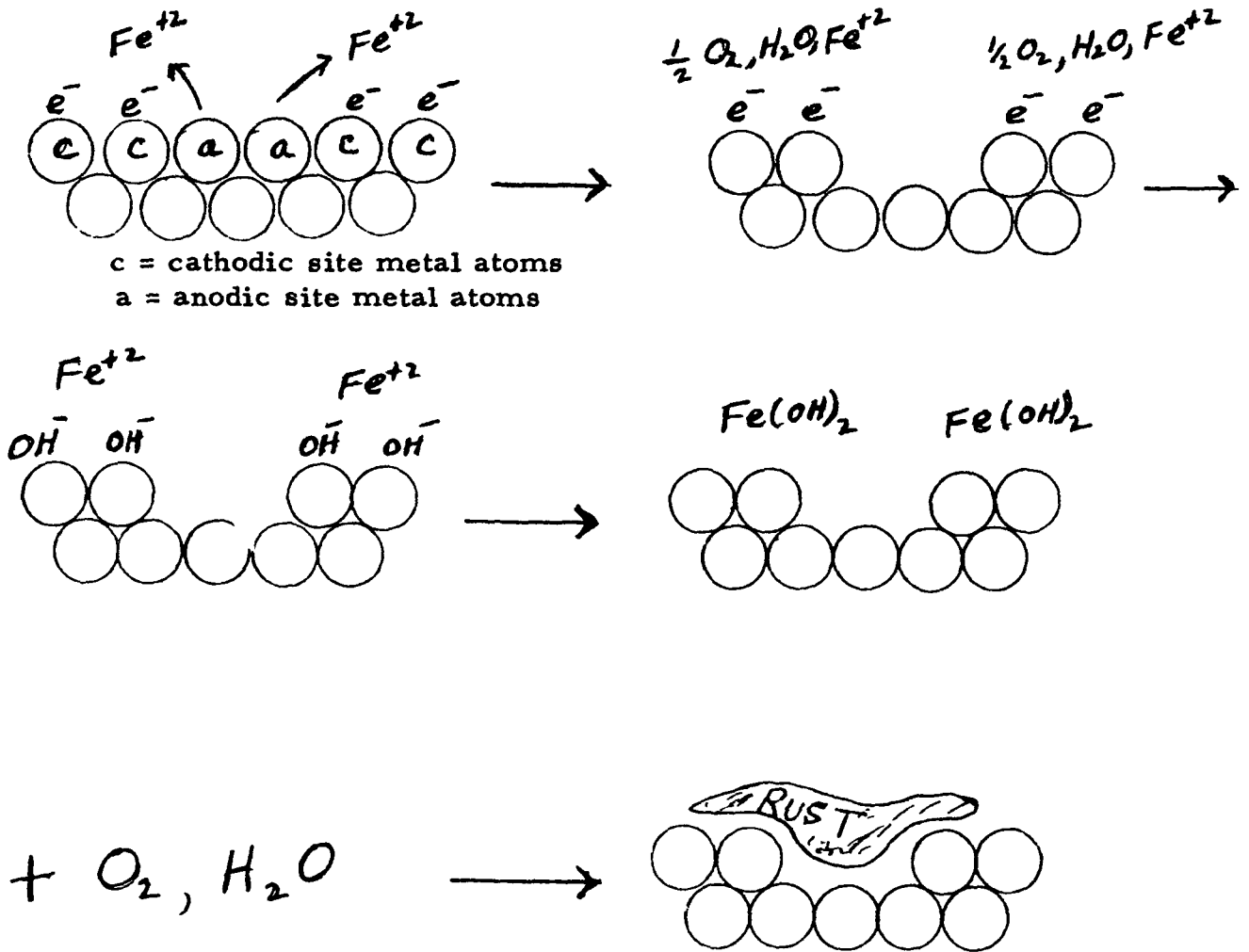
RUST = $Fe_2O_3 \cdot x\, H_2O$, $Fe_3O_4 \cdot y\, H_2O$, FeOOH, etc.

Figure 2   A Model of the Rusting Mechanism
XXV-2

The cathode reaction occurring is the one that produces the highest cathodic current (or electron flow to the cathodic sites) for the given conditions. Usually in the presence of air a solution above pH 5 contains sufficient dissolved oxygen to support reaction (2) or (3) above. In the vicinity of pH 7, hydrogen ion from water reduces at -0.41 volts while O_2 has a reduction potential of -0.83 volts (neglecting overvoltage). Therefore, the oxygen is reduced producing OH^- ions. (The reduction of water also forms OH^- ions.) Below pH 5 the cathode reaction is mainly hydrogen evolution.

Electrochemical Theory

For a spontaneously corroding metal surface not connected to an external electrical device, the anodic current, i_a, must equal the cathodic current, i_c. Since the anodic current is from the dissolution of the metal atoms it is also called the corrosion current, Icorr. The corrosion current sometimes is referred to as the exchange current, i_{ex}.

The corrosion current is an important quantity because it yields the actual rate at which the metal dissolves or forms corrosion product. The following relationships show the uses of Icorr: A corrosion current of 1 amp corrodes about 22 pounds of iron in one year; an actual corrosion rate calculated from data for aluminum corroding in corrosive water in the presence of Mobay inhibitor with an Icorr of 0.00785 microamps yields a corrosion rate of 0.00345 mils per year. Equations 6, 7, and 8 show how Icorr can give a corrosion rate.

6. $\dfrac{\text{Icorr (amps)}}{\text{F (96500 coulombs/equiv.)}}$ = gram equivalents of metal corroding per second

7. Weight (grams/second) of corroding metal = $\dfrac{\text{Icorr (amps)}}{\text{F (96500 C)}}$ X gram equivalent weight of metal corroding

The commonly used equation that gives mils per year (mpy) of metal corroding is as follows:

8. Corrosion Rate (mpy) = $\dfrac{0.1288 \text{ X Icorr X gram equivalent weight of metal}}{\text{density of metal}}$

—Icorr in microamps/cm^2
—gram equivalent weight of metal in grams
—density of metal in grams/cm^3

The electrical potential of any corroding metal surface (without any external connections) is the potential at which the corrosion current is produced. It is called the corrosion potential, Ecorr. Ecorr always lies between the equilibrium potential for the metal/solution half-cell and the equilibrium potential for the electron acceptor/solution half-cell. (These equilibrium potentials are not the Standard Reduction or Oxidation Potentials commonly found in references and textbooks. They depend on the metal, its surface condition, and the solution contacting the metal.) Unlike Icorr, Ecorr can be directly measured and can provide limited information about the corrosion system. Generally relatively positive Ecorr's (-0.2 to -0.4 volts) indicate low rates of corrosion while more cathodic values of Ecorr (-.6 to 1.0 volts) indicate higher corrosion rates for the metal surface. In an oft-quoated paper, Wormwell and Brasher' reported for painted steel that Ecorr initially dropped, then rose, to a maximum before finally dropping to permanent low values after fifty days (Ref. 1).

A more negative or cathodic potential applied externally accelerates the cathodic reaction. Likewise causing the potential to be more positive than Ecorr increases the anodic current. Figure 3a shows the current-over-potential relation for the general metal dissolution equilibrium. As shown on the left-hand side of Figure 3b (left of the zero current ordinate), an increasingly negative voltage departing from the equilibrium value for the cathodic site, produces an increase in the cathodic current.

If a metal/solution half-cell or electron-acceptor/solution half-cell are at some potential other than their equilibrium potential, they are said to be polarized. Therefore the two half-cells (one the cathodic site and the other the anodic site) are always polarized during the corrosion process. Since the cathodic and anodic sites are probably close on the metal surface, they are said to be at the same potential which is called the corrosion potential, Ecorr.

For a short-circuited non-connected corrosion cell

$$i_c = i_a = \text{Icorr}$$

and net current $= |i_c = i_a| = \Delta i$ and at Ecorr, $\Delta i = 0$.

If an external potential is applied to the metal surface to make it more positive or negative than the Ecorr of the corrosion, the polarization of the cell is altered and a net anodic or cathodic current can be observed. Overpotentials more positive than Ecorr increase the anodic current, while those less positive increase the cathodic current.
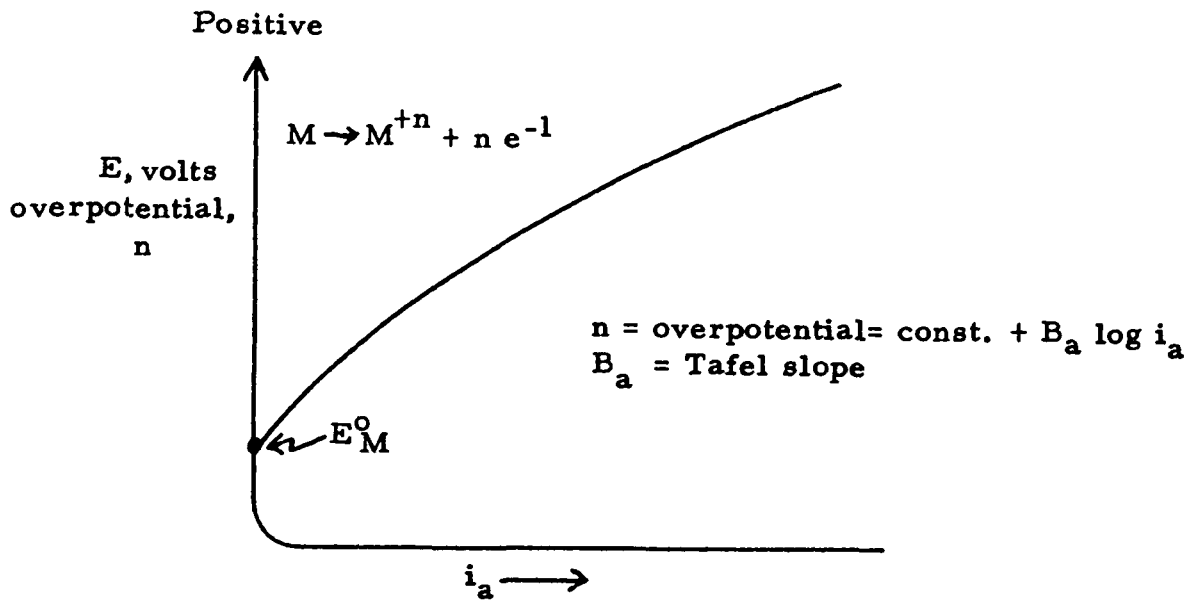
Positive

E, volts
overpotential,
n

$M \rightarrow M^{+n} + n\ e^{-1}$

n = overpotential= const. + $B_a \log i_a$
B_a = Tafel slope

E^o_M

$i_a \longrightarrow$

Figure 3a. The Anodic Current-Overpotential Diagram

Positive

E^o_A

$M \rightarrow M^{+n} + n\ e^{-1}$

$A + n\ e^{-1} \rightarrow$ Products

i_c

i_a

E_{corr}

E^o_M

$\longleftarrow i_c$ O   Icorr $i_a \longrightarrow$

Figure 3b. Cathodic and Anodic Relations
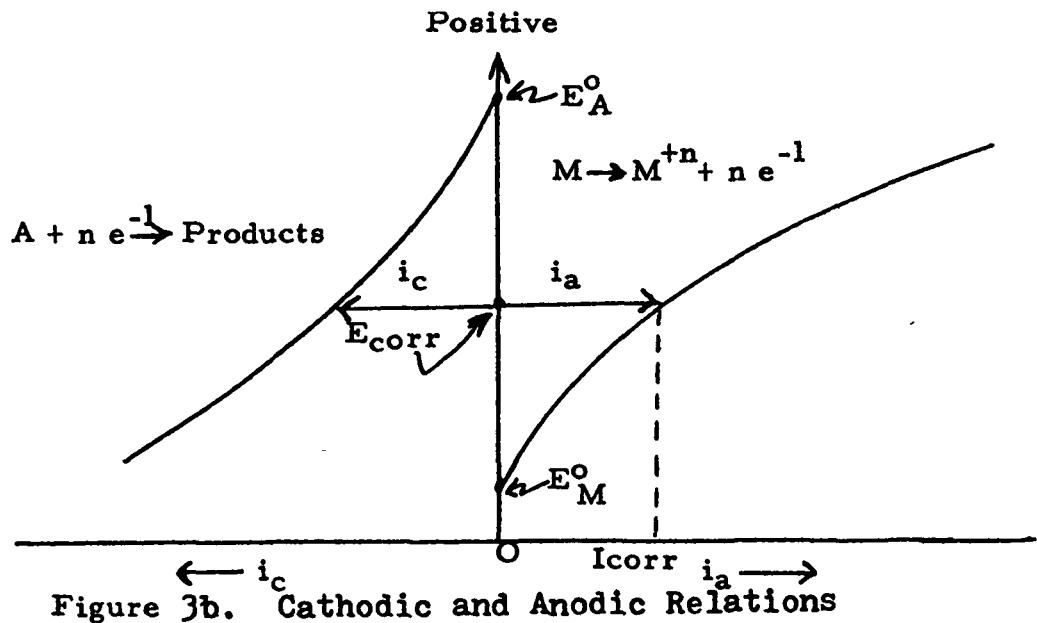
Summarizing, if E≠Ecorr, $\Delta i \neq 0$ (E = applied or imposed potential.)

for (E-Ecorr) >0, $i_a > i_c$ (anodic polarization)

for (E-Ecorr) <0, $i_c > i_a$ (cathodic polarization)

The difference between the imposed potential, E, and Ecorr is called overpotential, n, also labeled ΔE.

So, Eapplied - Ecorr = n = ΔE = overpotential

Development of the Resistance Polarization, Rp, Equation

The challenge of electrochemists studying corrosion is to obtain values for Icorr or io, the corrosion current density. Once obtained the values are easily converted to a corrosion rate by equation 8. About eighty years ago Tafel in studying hydrogen overvoltages on various metals formulated empirical equations (since then derived on theoretical bases) relating the overvoltage to current and exchange current. At Ecorr the exchange current density equals the corrosion current density, i_o.

Tafel's equation's:

$\Delta E = + B_c \log i_c/i_o$ (cathodic overpotential)

$\Delta E = - B_a \log ia/io$ (anodic overpotential)

B_a, B_c = Tafel slopes of ΔE vs. log i / io plots

$i_c/i_o = e^{2.3\ \Delta E/B_c}$, $i_a/i_o = e^{-2.3\ \Delta E/B_a}$

Δi = net current caused by overpotential, ΔE.

$\Delta i = |i_c - i_a| = i_o\ (e^{2.3\Delta E/B_c} - e^{-2,3\Delta E/B_a})$

Since $e^x = 1 + x + x^2/2! + \ldots$

$\Delta i = i_o\ (1 + 2.3\Delta E/B_c - 1 + 2.3\Delta E/B_a)$

$= i_o\ (2.3\Delta E)\ (B_a + B_c\ /\ B_c B_a)$

So, $i_o = \dfrac{\Delta i}{2.3\Delta E}\left[\dfrac{B_c\ B_a}{B_c + B_a}\right]$

This last equation is the Stern-Geary Equation and applies only when Activation Polarization exists. Concentration polarization must not be important. This is usually the case when the applied overpotentials and resultant currents are small enough to not affect species concentrations at the metal surface.

Dividing the overpotential by the net current gives the polarization resistance, R_p: $\Delta E/\Delta i = R_p$

Thus, $R_p = B_c B_a / 2.3 i_o (B_a + B_c)$. ($i_o = Icorr/cm^2$.)

So, Rp provides a pathway to the important parameter, i_o.

It is seen that R_p is the derivative of the potential at Ecorr with respect to the observed current. For this derivative or slope to be accurate, a straight line rela-tionship at Ecorr should exist at small overpotentials which is usually the case. R_p is inversely proportional to Icorr and the corrosion rate which means the more pola-rized the metal surface is at Ecorr the lower the rate of metal dissolution and corrosion.

Danford and Higgins (Ref. 2) and Mansfeld (Ref. 3) point out that a computer program named POLCUR can carry out effective non-linear least squares evaluation of over-potential-current data and produce accurate values for R_p, the Tafel slopes, Icorr and Ecorr. In this research it was assumed that the POLCUR treatment of the data and the subsequent computer calculations produced valid and relia-ble results. Occasionally data would not compute; this occurred usually at high corrosion currents. Sometimes this problem was remedied by adjusting the overvoltage range scanned from ±20 mV to ±10 mV.

The instrument used in the research would determine R_p and calculate Icorr and corrosion rate. Tafel slopes were keyed in at assumed values of 100 mV/decade along with area, equi-valent weight and density of the metal being studied. These instrument calculations were disregarded in nearly case in deference to the POLCUR results.

The measuring instrument was an EG&G Princeton Applied Research Model 350 Corrosion Measurement Console. This instrument and related information are described in Danford and Higgins paper (Ref. 2).

OBJECTIVES

The main objectives of the research were to determine if the Model 350 could be used to study the corrosion protection afforded by a thin layer of grease on a metal surface and if so, to evaluate and compare protection provided by two versions of Conoco grease on 4130 steel. If the electrochemical method proved successful in the initial investigations of grease-coated metal surfaces, then protection by a Texaco grease was to be determined.

Finally, an electrochemical study of the rate of corrosion inhibition of aluminum was to be investigated.

RESULTS AND DISCUSSION

1. Conoco grease studies. The purpose of this particular research was to compare the corrosion protection given by two Conoco greases used on metal joint surfaces of the SRB. The two greases differ slightly in their formulation; the "old" grease was used before January, 1983, and the "new" grease after this date. It was known that the "old" grease was effective and the question was can any difference in protective capability be detected electrochemically. The "new" grease is Conoco HD Calcium Grease No. 2.

To prepare the samples used in the corrosion measurement cell, 9/16 inch diameter by 1/16 inch thick 4230 steel discs were punched out, fine wet-sanded, degreased, and sprayed with a solution or suspension of the grease in trichloroethane. Sufficient spray passes deposited two mils of grease layer on the metal surface.

Following air drying three days, four discs were prepared, two with the "old" grease and two with the "new" grease formulation. They were placed in the corrosion measurement cell that contained 3.5% NaCl at pH 8.2. Alternate day measurements of Ecorr and ohmic resistance (Runc) were made plus the polarization-resistance scan if a measureable cathodic current was obtained. Only one sample of the "old" grease and one sample of the "new" grease provided a corrosion current. The other samples of each grease gave no corrosion current for the one month duration of the experiment. The corrosion rates calculated from these corrosion currents are shown in Figure 4.

Also graphed in this figure is the change of the ohmic resistance of the samples that occured with time. Of particular interest was the increase in resistance observed after about

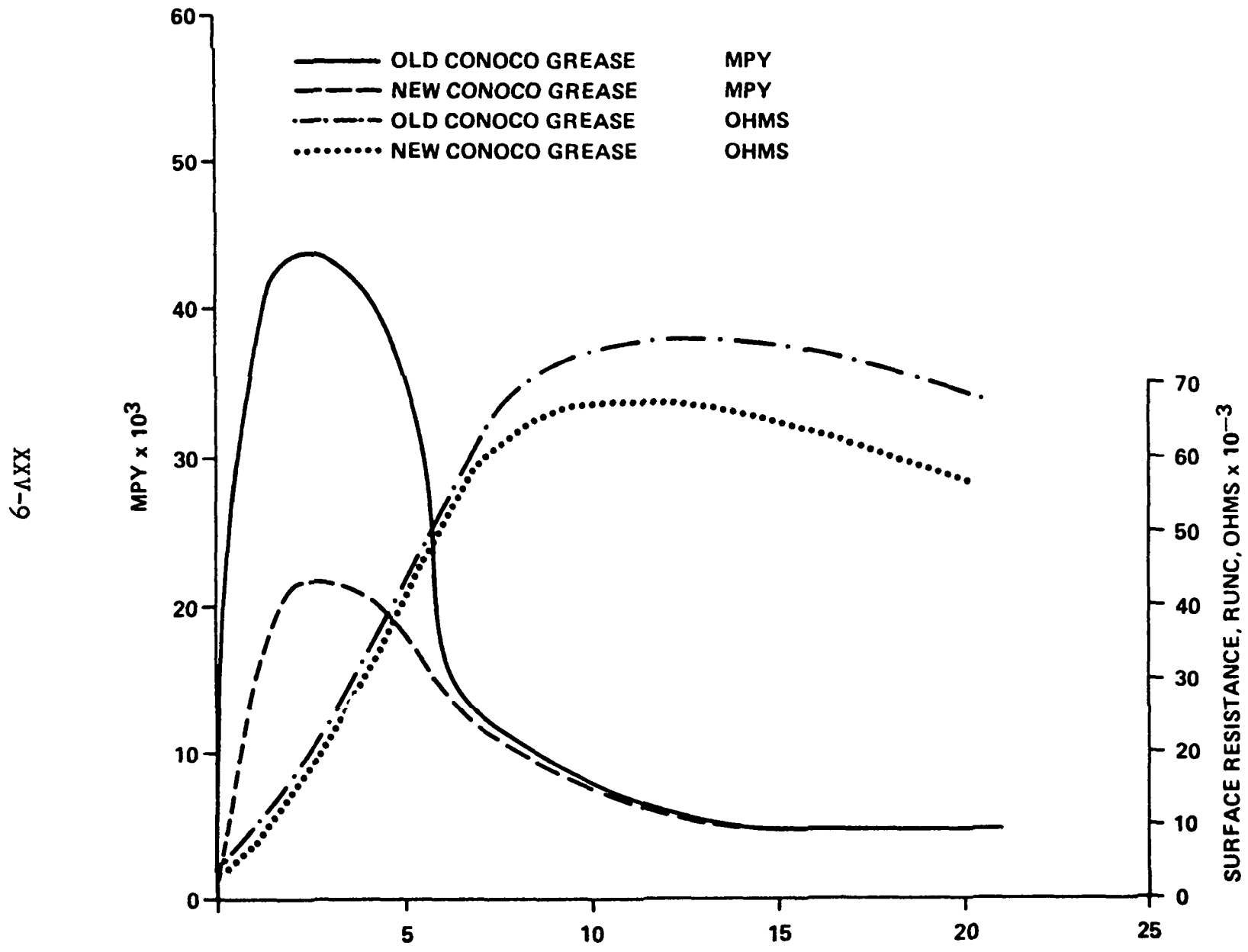CORROSION RATES AND RESISTANCES OF 4130 STEEL
COATED WITH 2 MIL GREASE

Figure 4

	OLD GREASE	NEW GREASE*
Ca^{++}(mg/g) (deionized water)	1.22	0.32
Ca^{++}(mg/g) 3.5% NaCl	2.94	2.60
Na^+ (mg/g) (Deionized water)	0.017	0.249

*Conoco HD Calcium Grease No. 2 currently used on SRB

Notes:
1. No dedectable lead in any grease samples.
2. No zinc analysis performed.
3. Anion analysis complete at this time, but more chloride being found in New grease than in Old grease. Also, the sulfonate content of each grease reported to be similar.

Table 1. Cations Leached from Conoco Grease in Two Weeks

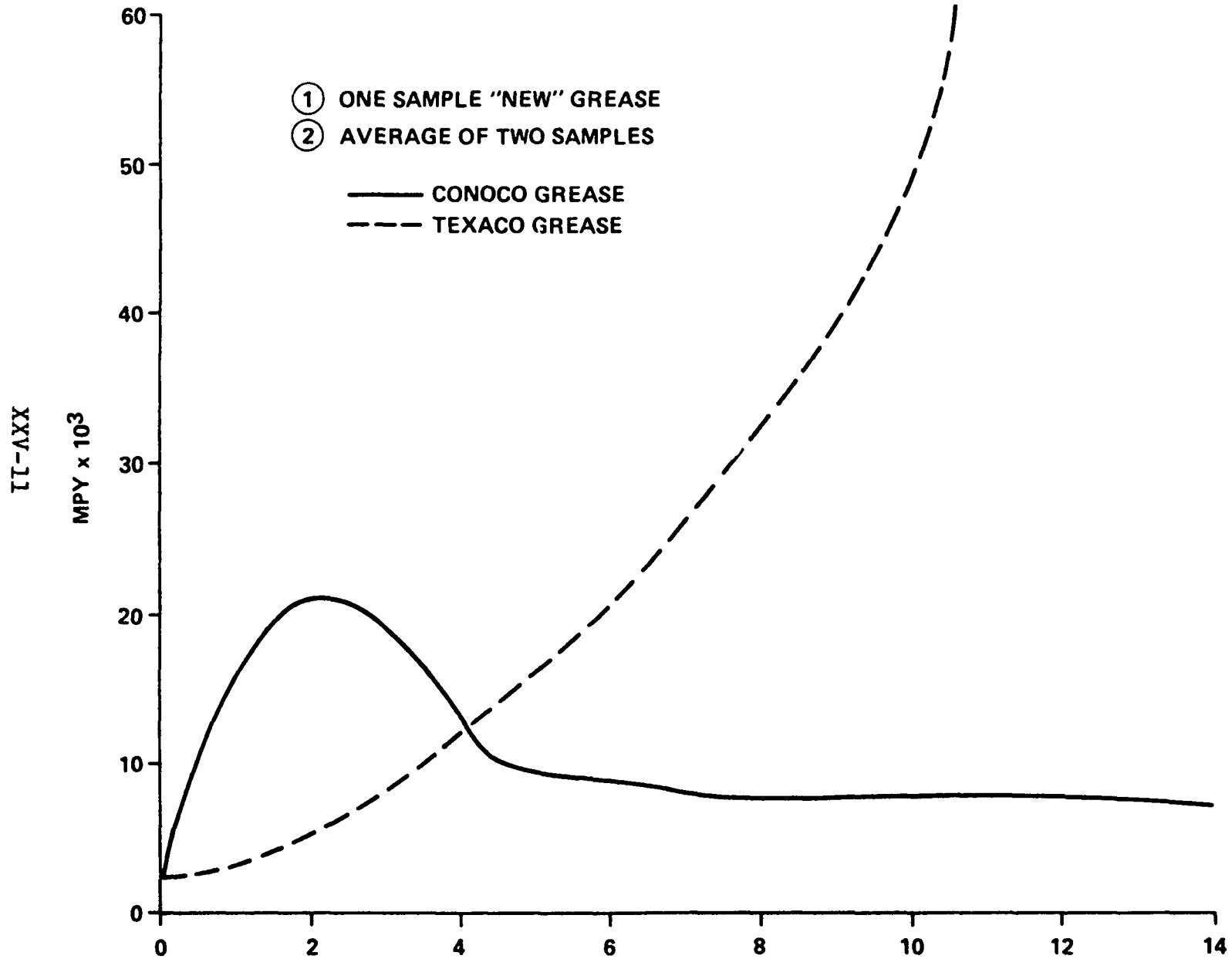COMPARATIVE CORROSION RATES OF 4130 STEEL WITH 2 MILS CONOCO GREASE① AND TEXACO GREASE②

Figure 5

DAYS IMMERSION IN 3.5% NaCl, PH 8.2

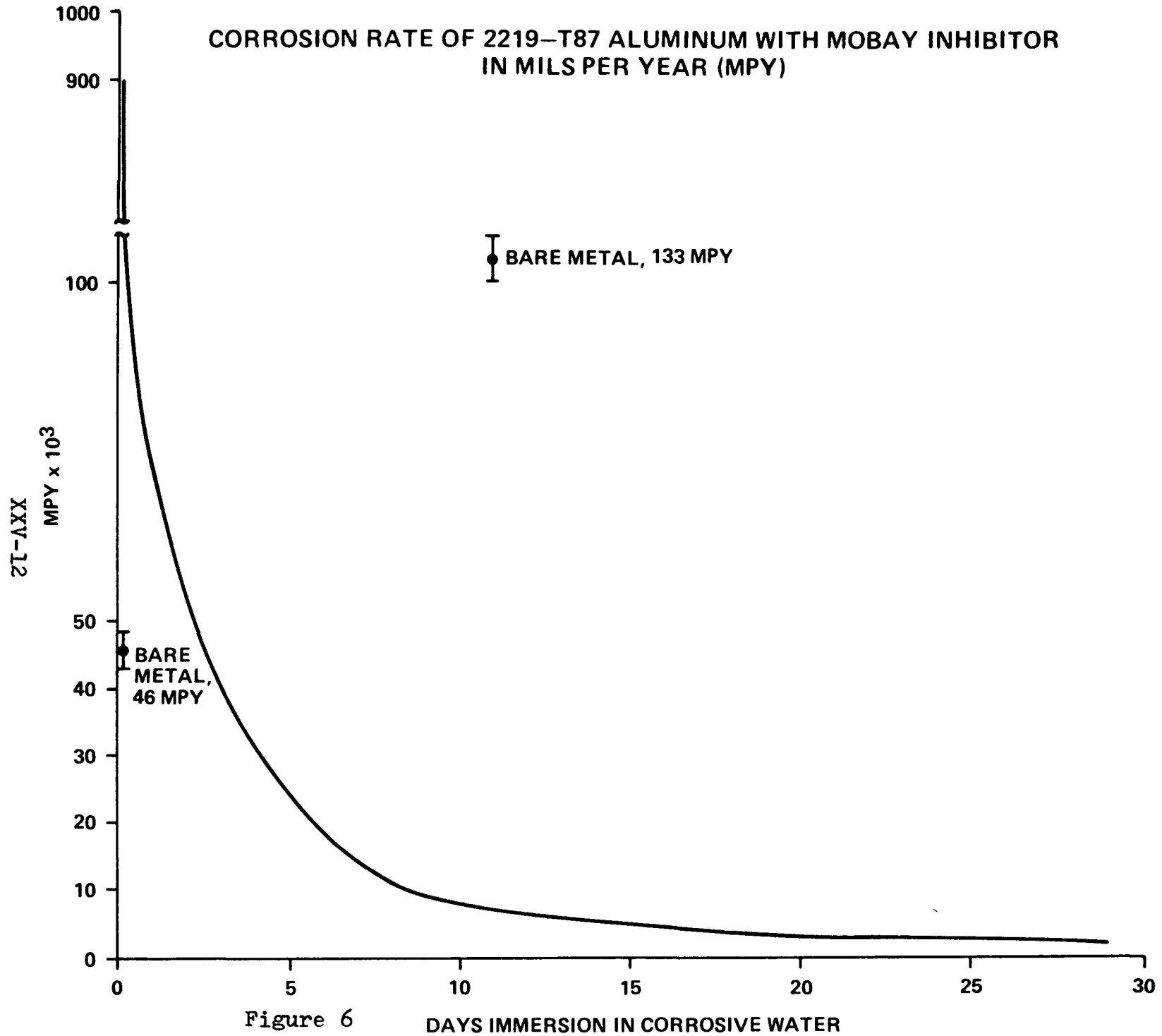CORROSION RATE OF 2219–T87 ALUMINUM WITH MOBAY INHIBITOR IN MILS PER YEAR (MPY)

Figure 6

DAYS IMMERSION IN CORROSIVE WATER

one week immersion in the 3.5% salt water. Analysis of solutions in contact with the greases for two weeks indicated significant concentrations of calcium ions as shown in Table 1. Most likely the loss of ions from the greases increased their electrical resistance. In the salt solution an ion-exchange mechanism probably occurs; the solubility of the resulting calcium hydroxide increases because of the high ionic strength (of the salt solution) according to the Debye-Huckel Theory.

2. Texaco grease study. Because Texaco Regal AFB-2 grease was known to be comparatively ineffective in preventing steel corrosion, it was thought useful to examine this grease electrochemically. Two samples of the grease on 4130 steel were prepared as described above. The results indicated that one sample showed fairly good resistance to salt water corrosion, while the other sample produced relatively high corrosion currents after three days. An average corrosion rate calculated from the data from both Texaco samples is compared to Conoco grease coated samples in Figure 5.

3. Aluminum corrosion inhibition study. Research reported in 1978 showed that Mobay OC 2002 Inhibitor gave excellent aluminum protection (Ref. 4). A subsequent electrochemical study showed that the same inhibitor decreased the corrosion rate very little (Ref 5).

A thirty day experiment showed a high initial rate of corrosion that rapidly decreased in about one day, reaching very low rates in about five days. Figure 6 pictures this change. Obviously an "induction period" is needed for the protection mechanism to occur on the metal surface.

4. Seawater inhibition of steel and aluminum corrosion. Various reports over many years point out that seawater contains inhibitors that lessen immersed steel and aluminum corrosion. A brief electrochemical investigation to verify (at least superficially) these reports was conducted using artificial sea water prepared from ASTM Sea-Salt (42.0 grams/liter solution, pH 9.0).

Aluminum (2219-T87) showed significant protection in the seawater with a corrosion rate of about 0.01 mpy. In 3.5% NaCl solution at the same pH the aluminum corroded at a rate of 2 mpy.

Similar experiments with 1010 and 4130 steels indicated no difference of corrosion rate in the artificial seawater and 3.5% salt solutions.

5.   Effect of magnesium ions on steel and aluminum corrosion. A brief study to determine the difference in corrosion rates for 4130 steel and 2219-T87 aluminum in 3.5% NaCl and 2.86% NaCl/0.52 $MgCl_2$ solutions was conducted.

At pH's 4.9, 6.9, and 8.9 no inhibition of steel corrosion by the magnesium was observed. (A sample of 1010 steel, however, did show about a 50% reduction in corrosion at pH 8.9 with magnesium ions present).

Although the large variation of corrosion currents with the aluminum makes definite conclusions impossible, a three to four-fold decrease in corrosion at pH 4.9 was observed.

6.   Effect of two chelating species on steel corrosion rates. In as much as oxalate and ethylenediammine tetraacetic acid (EDTA) are excellent chelating species for Fe^{2+} ions, it was hypotehsized that these two species would accelerate corrosion by solubilizing the dissolving iron and prevent a protective rust coating from forming.

This was verified by 1010 steel showing a 40% increase in corrosion rate in corrosive water 0.01 M in oxalic acid and a 90% increase in the same medium containing 0.01 M EDTA.

CONCLUSIONS

1. The electrochemical polarization-resistance method utilizing the Model 350 Corrosion Measurement Console is an effective means of determining corrosion rates of grease coated steel surfaces.

2. Conoco HD Calcium Grease #2 was shown to be as effective as the Conoco grease used before January, 1983 on the SRB joints in limiting corrosion rates on 4130 steel surfaces immersed in 3.5% NaCl, pH 8.2.

3. Conoco HD Calcium Grease #2 was shown to provide greater corrosion prtotection than Texaco Regal AFB-2 Grease on 4130 steel surfaces immersed in 3.5% NaCl, pH 8.2.

4. Mobay OC 2002 aluminum corrosion inhibitor provides excellent corrosion protection for 2219-T87 aluminum.

5. The corrosion of aluminum is inhibited to a significant degree in an aqueous environment that contains Mg^{++} ions.

6. Oxalic acid and ethylenediamminetetraacetic acid both accelerate the corrosion rate of 1010 steel in an aqueous environment.

RECOMMENDATIONS

1. The corrosion rates of nickel and nickel alloys in ammonia and hydrazine solutions be examined electrochemically by the polarization-resistance method.

2. At least two more corrosion measurement cells should be purchased by EH 24 in order that more concurrent investigations can be conducted.

3. The POLCUR computer program should be examined to determine the reason(s) that it does not process some polarization-resistance data effectively.

4. An extended investigation should be conducted on the effect of dissolved chelating agents on the corrosion rates of various metals.

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