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INHIBITION OF CORROSION IN CATAPULT WATER BRAKE TANKS

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28 January 1976

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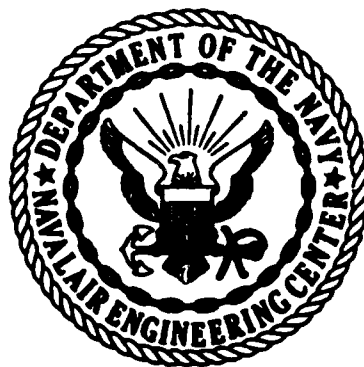
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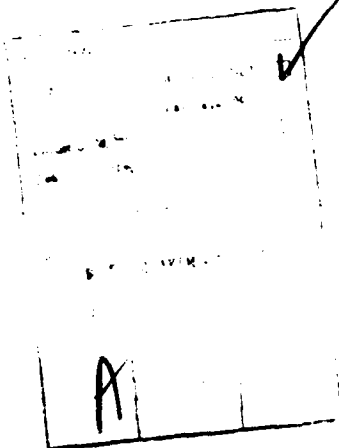
INHIBITION OF CORROSION
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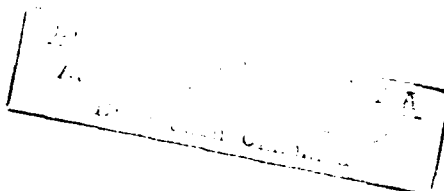
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testing under simulated conditions to determine methods for reducing crevice corrosion, characterize stress corrosion susceptibility, and optimize inhibitor treatment.

The results of the program overwhelmingly favor initiation of inhibitor treatment of catapult water brakes on other ships. Sodium nitrite inhibitor treatment will virtually eliminate corrosion of the water brakes thereby improving safety, increasing reliability and reducing maintenance costs. Before initiating inhibitor treatment on a fleetwide basis, additional work is required to determine proper procedures for procurement, containment and storage of the inhibitor; to assess environmental implications; and to gather data on the required inhibitor concentration as a function of brake water salinity.

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I. INTRODUCTION

In 1968, NAVAIRENGCEN undertook a study to determine the feasibility of using sodium nitrite as a corrosion inhibitor in catapult water brake tanks. The initial study yielded favorable results, therefore follow-up work was initiated to gather additional laboratory data as well as evaluate the sodium nitrite inhibitor on an operational aircraft carrier. The laboratory study included testing under simulated conditions to determine methods for reducing crevice corrosion, characterize stress corrosion susceptibility, and optimize inhibitor treatment. This report presents the results of the program.

II. SUMMARY

The results of the program overwhelmingly favor initiation of inhibitor treatment of catapult water brakes on other ships. Sodium nitrite inhibitor treatment will virtually eliminate corrosion of the water brakes thereby improving safety, increasing reliability and reducing maintenance costs. Before initiating inhibitor treatment on a fleetwide basis, additional work is required to determine proper procedures for procurement, containment, and storage of the inhibitor; to assess environmental implications; and to gather data on the required inhibitor concentration as a function of brake water salinity.

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VI. INHIBITION OF CORROSION IN CATAPULT WATER BRAKE TANKS

A. INTRODUCTION. NAVAIRENGCEN commenced in 1968 to investigate the feasibility of using sodium nitrite as a corrosion inhibitor in two distinctive environments

1. Sea water / sea air and detergents as used for flight deck washing at ambient temperatures.
2. Low salinity water / sea air at a maximum temperature of 180°F, as encountered in the catapult water brake tanks.

The initial studies showed favorable results, particularly concerning the catapult water brake tanks. This led to follow-on investigations which yielded many favorable results. Almost without exception, investigations indicated that the effects of the use of sodium nitrite in the catapult water brake system would be beneficial. Under simulated water brake conditions, the investigations showed that sodium nitrite at a concentration of about 1.25% will:

1. Reduce the rate at which exposed surfaces of SAE 4340 steel corrode to essentially zero.
2. Reduce the rate at which many copper and nickel bearing alloys corrode; and reduce the probability of plug-type dezincification of brasses.
3. Reduce the rate of corrosion caused by different metals in contact with each other.
4. Maintain its inhibiting effectiveness for at least a 3-month period with a reasonable depletion rate.

While corrosion in tight crevices was not reduced nearly as much as that on exposed surfaces, there was good reason to believe that this situation could be improved. The overall results of the initial program justified a full scale evaluation of the use of the inhibitor in the water brake tank, concurrent with further laboratory testing regarding optimization of inhibitor treatment and susceptibility to stress corrosion cracking.

As a result NAVAIRENGCEN initiated further work, the scope of which follows:

1. Conduct a controlled evaluation of sodium nitrite as a corrosion inhibitor in an operational aircraft carrier water brake system.
2. Conduct additional laboratory research on pH treatment as a means of modifying the inhibitor to further reduce crevice corrosion.

3. Characterize the stress corrosion cracking properties of the steels specified for fabrication of the various contaminants that may enter the water brake system, including sodium nitrite, sodium nitrate, and sea water.
4. Conduct additional laboratory research on wetting agents and/or other inhibitors that might be used in conjunction with or instead of sodium nitrite to optimize corrosion inhibition in the water brake system.

The following is a report of this work.

B. LABORATORY STUDIES

1. EXPERIMENTAL PROCEDURES

a. EFFECT OF PH TREATMENT ON CORROSION IN CATAPULT WATER BRAKE SYSTEMS. PH treatment was investigated primarily as a means of reducing crevice corrosion which occurs even in the presence of the sodium nitrite inhibitor. At the same time, possible adverse effects of pH treatment on bi-metallic corrosion and stress corrosion were also studied. The experimental approach follows:

(1) CREVICE CORROSION - HYPOTHETICAL MODEL. In a corrosion reaction, the polarization behavior of the anode and cathode making up the cell controls the kinetics or rate of reaction. The electrochemical difference between the anode and cathode represents the thermodynamic driving force of the reaction. In the case of a crevice, the metal within the crevice usually acts as the anode in the electrochemical cell and the metal outside the crevice acts as the cathode. By simulating environmental conditions as they would exist at the anode and cathode, potential and polarization characteristics can be experimentally determined and corrosion rates predicted by use of a theoretical model.

The present program studied the effect of pH treatment on crevice corrosion in an inhibited water brake system, by investigation of six different experimental conditions as follows:

- (a) .2% salinity water, 180°F, 1.25% NaNO_2 , air sat'd, pH = 8 @ ambient
- (b) .2% salinity water, 180°F, 1.25% NaNO_2 , air sat'd, pH = 10 @ ambient
- (c) .2% salinity water, 180°F, 1.25% NaNO_2 , air sat'd, pH = 12 @ ambient

- (d) .2% salinity water, 180°F, no inhibitor, O₂ depleted, pH = 8 @ ambient
- (e) .2% salinity water, 180°F, no inhibitor, O₂ depleted, pH = 10 @ ambient
- (f) .2% salinity water, 180°F, no inhibitor, O₂ depleted, pH = 12 @ ambient

Condition (a) represents the water brake environment outside a crevice without pH treatment while condition (d) represents the area inside the crevice without pH treatment. Previous work by NAVAIRENGCEN showed that the primary cause of crevice corrosion in the presence of the sodium nitrite inhibitor was inhibitor depletion in tight crevices. Conditions (b) and (c) represent the area outside a crevice with the pH of the brake water adjusted to the values listed. In the same way, conditions (e) and (f) represent the environment within the crevice with pH treatment.

A polished (600 silicon carbide grit finish), degreased steel (SAE 4340) coupon was immersed under each of the experimental conditions listed. After a 24-hour stabilization period, potential and polarization measurements were made. Figure 1 shows a schematic of the instrumentation used to gather the data. Intersection of the cathodic polarization curve for the solution condition outside the crevice and the anodic polarization curve for the solution condition inside the crevice determines the galvanic corrosion current that would flow in the hypothetical cell. Polarization resistance measurements determine the local-action corrosion that would occur within the crevice. Appendix A describes the calculation of local-action corrosion rates from polarization resistance measurements. The total corrosion rate within the crevice is the sum of the galvanic corrosion rate and the local-action corrosion rate.

(2) CREVICE CORROSION - SIMULATED EXPOSURE TESTS. Test coupon assemblies as shown in Figure 2 were exposed for 3 months under simulated water brake conditions as follows:

- (a) .2% salinity, 1.25% NaNO₂, O₂ sat'd, 180°F, no pH treatment (pH = 8)
- (b) .2% salinity, 1.25% NaNO₂, O₂ sat'd, 180°F, pH = 10
- (c) .2% salinity, 1.25% NaNO₂, O₂ sat'd, 180°F, pH = 12

The test coupon assembly is designed to produce typical crevice corrosion that would occur in a water brake system as well as the local-action corrosion, by itself, that would occur in a crevice. An SAE 4340 steel coupon (1" x 1/2" x 1/16") is mounted on one side between teflon washers creating crevices at each washer. If the simulated water brake environment stimulates crevice corrosion, it should be evident at the teflon washer-steel interface. In addition, a small steel coupon (SAE 4340 - 1/4" x 1/4" x 1/16") is embedded in the teflon mounting block as shown. This steel coupon is then covered by a teflon coupon so that the entire steel coupon is within the crevice formed between the teflon block and teflon coupon. The only corrosion is local-action corrosion within the artificial crevice.

Previous research indicated that corrosion occurs only in extremely tight crevices where the nitrite inhibitor becomes depleted; therefore, the surface finish on the small coupon was varied in order to experimentally vary the crevice opening. The different surface profiles (peak to valley) included in the test were:

- (a) .12 mils
- (b) .08 mils
- (c) <.04 mils

(3) BI-METALLIC CORROSION. The effect of pH treatment on bi-metallic corrosion was predicted by using an approach similar to that used in the crevice corrosion phase of the investigation. Differences between alloys result in corrosion cell potential differences that cause bi-metallic corrosion; differences between solution conditions result in the cell potential differences that cause crevice corrosion.

Simulation of the environment and determination of the potential and polarization characteristics for each alloy in the environment provided data for estimating the effect of pH treatment on bi-metallic corrosion. Electrochemical measurements were made on the other alloys used for hardware in the water brake system. Table 1 lists these alloys. The measurements were made with the instrumentation setup shown in Figure 1 under the following solution conditions:

- (a) .2% salinity, 1.25% NaNO_2 , O_2 sat'd, 180°F, no pH treatment (pH $\approx$ 8)
- (b) .2% salinity, 1.25% NaNO_2 , O_2 sat'd, 180°F, pH $\approx$ 10
- (c) .2% salinity, 1.25% NaNO_2 , O_2 sat'd, 180°F, pH $\approx$ 12

b. **STRESS CORROSION CRACKING SUSCEPTIBILITY IN CATAPULT WATER BRAKE SYSTEMS.** A test procedure developed by Brown¹ was used to determine the stress corrosion susceptibility of two steel alloys presently used in fabricating water brake cylinders. The test utilizes a single-edge, notched, pre-cracked specimen stressed in bending as a cantilever beam. The intentional crack in the test specimen obviates the waiting period required for formation of a "natural" stress raiser such as a corrosion pit. The crack also provides a stress raiser in a form that can be treated by equations from linear elastic fracture mechanics. The following equation derived from fracture mechanics enables calculation of the stress intensity at the crack tip:

$$K_I = 4.12 M[1/\alpha^3 - \alpha^3]^{.5} \div BD^{1.5}$$

where,

K_I = stress intensity, ksi [in]^{.5}

M = bending moment at notch, in-kilopounds

B = horizontal thickness of the specimen, in.

D = vertical depth of the specimen, in.

α = $1 - a/D$

a = total initial depth of fatigue crack, in.

As is evident, stress intensity depends not only on the nominal stress in a metal but on the size and geometry of a crack-type flaw. Fracture mechanics theory postulates that stress intensity and not nominal stress determines whether a crack will propagate.

According to Brown's test method, the stress intensity required for fracture of a given alloy in air is first determined. This quantity, identified as K_{Ix} , serves as a reference point characterizing the response of the alloy to stress in the absence of corrosion. The stress intensities, K_{Ii} , required for rupture in the corrodent of interest are then determined. These data are gathered over time-to-break periods up to 1000 minutes. The stress intensities, k_{Ii} , required for fracture in the corrodent will be lower than the stress intensity, K_{Ix} , required for fracture in air if a given alloy is susceptible to stress corrosion cracking in the corrodent. Figure 3 shows a typical plot for data gathered according to this test method.

Figure 4 shows a typical test specimen. Initially, a sharp notch is machined across the mid-length of the specimen. A fatigue crack is then initiated at the root of the notch by fatiguing the specimen in a machine lathe. To do this, one end of the test specimen is held in a tool post and the other bears against a steel ball eccentrically mounted in the lathe chuck. The crack is propagated to a depth approximately .17 to .25 of the distance measured from the root of the notch to the base of the specimen.

Figures 5 through 7 show the general arrangement for the test. Flowing test solution contained in a flexible reservoir surrounded the pre-cracked area. Glass-reinforced phenolic spacers thermally insulated the test specimen from the test rig at all contact points. Insulating the test specimen removed the test rig as a heat sink, keeping the temperature of the test specimen identical to that of the test solution. This is an important experimental parameter considering that the typical water brake environment approaches 180°F operating temperatures.

The steel alloys which were examined included SAE 4340, typical properties of which are shown in Table II, and the steel alloy presently specified by NAEC-MPR-12. NAVAIRENGCEN originally specified the SAE 4340 steel alloy for water brake cylinders however changed the MPR-12 specification to cover another alloy which has superior impact toughness. Table III summarizes mechanical properties specified as a minimum in the revised MPR-12 specification.

Stress intensity versus time-to-failure curves were developed under exposure to seven different conditions:

- (1) Air, 80°F, 50% R.H.
- (2) Water, 180°F, .2% salinity, no pH treatment
- (3) Water, 180°F, .2% salinity, 1.25% sodium nitrite, no pH treatment
- (4) Water, 180°F, .2% salinity, 1.25% sodium nitrite, pH = 12
- (5) Water, 180°F, .2% salinity, 1.25% sodium nitrate, no pH treatment
- (6) Water, 180°F, .2% salinity, 1.25% sodium nitrate, pH = 12
- (7) Water, 180°F, .2% salinity, ethylene glycol contamination, no pH treatment

Sodium nitrate was included because it was thought that the sodium nitrate might be a by-product of the inhibition reaction and possibly cause stress corrosion cracking.

c. OPTIMIZATION OF INHIBITOR TREATMENT. A literature search was conducted to determine other inhibitors and wetting agents that might be used to optimize inhibitor treatment in the water brake system. The literature search included a review of available technical literature and manufacturer's published data. Based on the results of this literature search, 23 inhibitor "systems" were screened in simulated water brake solutions (.2% salinity, 180°F). The

screening tests were conducted by measuring the rate at which an SAE 4340 steel coupon corroded in the presence of the candidate inhibitor system. The corrosion rates were measured by polarization resistance measurements after allowing 24 hours for stabilization in the inhibited solution. The three inhibitor systems in which the steel test coupon exhibited the lowest corrosion rate were selected for further study.

Further study included evaluation of the ability of three inhibitor systems to prevent crevice and bi-metallic corrosion. Experimental techniques similar to those previously described were employed.

2. DISCUSSION OF RESULTS

a. EFFECT OF PH TREATMENT ON CORROSION IN CATAPULT WATER BRAKE SYSTEMS.

(1) CREVICE CORROSION - HYPOTHETICAL MODEL. Figure 8 shows a composite plot of the electrochemical polarization and potential data acquired in this phase of the program. As is evident, increasing solution pH tends to decrease the potential difference in the hypothetical crevice corrosion cell assuming that the bulk solution pH is the same as the solution pH within the crevice. This is an unrealistic assumption however it does provide a fair indication of the relative effects of increasing the pH of the brake water. The net effect is a decrease in the galvanic corrosion current. Without pH treatment ($\text{pH} = 8$), the galvanic corrosion current is $26 \mu \text{ amps/cm}^2$. At $\text{pH} = 12$, the galvanic corrosion current is $.23 \mu \text{ amps/cm}^2$, a reduction of two orders of magnitude.

Table IV shows the local-action corrosion rates determined for the area within the crevice. The data of Table IV indicate that increasing the pH within the crevice reduces local-action corrosion. Figure 9 summarizes the crevice corrosion rates for each pH condition in the hypothetical model. Based on these results, pH treatment appears to be beneficial in reducing crevice corrosion in a nitrite-inhibited system. However, these results were determined by considering a hypothetical model with certain implicit assumptions. The results of actual exposure tests must be examined before drawing any firm conclusions.

(2) CREVICE CORROSION - SIMULATED EXPOSURE TESTS. Removal of the test coupons after 3 months simulated exposure indicated that treatment to a level of pH 10 yields marginal results. Figures 10 and 11 show typical results for coupons exposed in inhibited water brake solution without pH treatment ($\text{pH} = 8$) and coupons exposed in inhibited water brake solution at a pH of 10.

Crevice corrosion occurred on both sets of test coupons in tight crevices. The degree of surface polish on the test coupons did not have any noticeable effect.

Treatment to a level of pH 12, however, did reduce crevice corrosion susceptibility in nitrite-inhibited brake water. Crevice corrosion was observed in only a few instances on the test coupons. Figure 12 shows typical results.

A possible adverse effect of pH treatment is that above a pH of approximately 10, insoluble salts of calcium and magnesium precipitated. This resulted in scale formation on wetted surfaces. Loose scale flaking off of the tank wall could cause clogging of pump strainers.

(3) BI-METALLIC CORROSION. Laboratory tests indicate that pH treatment in a water brake system will not significantly affect bi-metallic corrosion. Figure 13 and Table V present the results of these tests. Figure 13 shows the effect of pH treatment on the corrosion potential of the different copper-bearing alloys in the water brake system as well as SAE 4340 steel. The effect of increasing pH in almost all cases is to shift the corrosion potential to more active (negative) values. The most significant observation regarding the effect of pH treatment on bi-metallic corrosion is that the relative differences in potential between alloys do not significantly change. This indicates that the thermodynamic driving force for the bi-metallic corrosion reaction has not been appreciably altered. There is a shift in the relative position for some alloys, however, this is still considered to be insignificant.

The effect of pH treatment on the local-action corrosion rates of the alloys is shown in Table V. For most alloys, it is apparent that adjusting the pH of the brake water to a level of 10 is beneficial - the corrosion rate is actually reduced. For all alloys except one (copper), increasing the pH level to 12 causes an increase in local-action corrosion rate. The magnitude of increased corrosion rate, however, does not seem adverse.

b. STRESS CORROSION CRACKING SUSCEPTIBILITY. Table VI presents the mean stress intensity required for fracture under each of the test conditions. From the data, several things are apparent regarding performance of the alloys in these environments. First, each alloy is susceptible to stress corrosion cracking in .2% salinity water @ 180°F. The mean stress intensity (K_{Ic}) required for fracture of the MPR-12 alloy in air was 121 ksi [in]^{.5}. In .2% salinity water @ 180°F, the mean stress intensity required for fracture was 111 ksi [in]^{.5}, 10 ksi [in]^{.5} lower than that for air. This reduction in stress intensity required for fracture is indicative of stress corrosion

susceptibility. The difference between the two means is significant at a confidence level of 96%.

Table VI shows that the SAE 4340 alloy is also susceptible to stress corrosion cracking. The mean stress intensity for air fracture was 90 ksi [in].⁵ as compared to a mean stress intensity for fracture in .2% salinity, 180°F water of 75 ksi [in].⁵. This difference is significant at a confidence level of 99%. Appendix B details the statistical analysis of the data.

Addition of sodium nitrite to the brake water eliminates the susceptibility of the MPR-12 alloy to stress corrosion cracking. The mean stress intensity required for fracture is almost the same as required in air. However, sodium nitrite inhibitor does not reduce the susceptibility of the SAE 4340 alloy to stress corrosion cracking. The mean stress intensity required for fracture is about the same as that in uninhibited brake water.

Data obtained for brake water treated to pH = 12, and for water contaminated with sodium nitrate and ethylene glycol shows that none of the afore-mentioned conditions significantly increases the susceptibility towards stress corrosion cracking over a .2% salinity water solution (typical brake water). For the SAE 4340 alloy, the mean stress intensity required for fracture in each of the water solutions was not significantly different. For the MPR-12 alloy, sodium nitrate at pH = 12 and ethylene glycol both eliminated stress corrosion susceptibility. The sodium nitrate without pH treatment and sodium nitrite at pH = 12 were no worse than the .2% salinity water, by itself.

c. OPTIMIZATION OF INHIBITOR TREATMENT.

(1) LITERATURE SEARCH. Table VII lists other inhibitors and wetting agents chosen for study in this phase of the program.

Nalco 439 is a product of the Nalco Chemical Co. and is a boron nitrite-organic formulation supplied in liquid form. It is intended for use in chilled water and hot water heating systems.

Emulsifier STH, a combination inhibitor and wetting agent, is a product of GAF Corp. It is a mepasin-sulfamido carboxylic acid in the form of a viscous liquid. When added to water it emulsifies immediately and gives the solution a milky appearance. It is used in acid pickling operations² as well as applications involving salt water, fuels and oil³. It inhibits corrosion by forming a tightly adherent film on the metal surface preventing contact with the corrosive environment.

Due to the high metal affinity of the Emulsifier STH, a water repellant film remains on the surface after the metal is removed from the fluid. This inhibitor might be advantageous as an additive to flight deck washdown solutions in controlling corrosion of deck hardware.

Calgon CS is a proprietary formulation manufactured by Calgon Corp. It is a synergistic combination of sodium nitrite-borax and organic inhibitors with a buffering agent. Supplied as a powder, it is designed for use in closed non-potable water systems. It is considered less toxic than chromates.

Polyrad 1100 A, a product of Hercules, Inc.⁴, is a wetting agent with some inhibiting properties in acid media. It is a viscous, oily solution, basically an oxyethylated amine. As mixed, it is considered relatively non-toxic⁵.

Dearborn 561 is a synthetic organic liquid manufactured by Dearborn Chemical Co. It forms a uniform barrier film on a metal surface and is considered non-toxic.

Sodium molybdate is an inorganic compound used in all kinds on non-potable water systems⁶. It is moderately toxic⁷.

Drewgard 100, a proprietary formulation of Drew Chemical Co., is a mixture of synthetic surface active organics which form a chelating-type protective film⁸. The manufacturer recommends it for a cooling waters and chloride brines. The inhibitor supposedly provides extended protection on a metal after removal from solution. It is non-toxic.

Betz Corr-Shield K7 is a nitrite-borate silicate combination produced by Betz Laboratories. It is designed for the treatment of closed water systems.

The literature search identified sodium benzoate as an organic inhibitor useful in controlling corrosion of iron in neutral or alkaline solutions containing chloride ions⁹. It is supposedly effective when used in conjunction with sodium nitrite¹⁰. It is slightly toxic⁷.

The literature also indicated maleic hydrazide and ferric ethylenediaminetetraacetic acid (EDTA) are effective in reducing the corrosion of steel in the presence of chlorides¹¹. Ferric EDTA is an inorganic and maleic hydrazide an organic inhibitor. Sodium phosphate and

[sodium hexametaphosphate are well documented inhibitors useful in controlling corrosion in water systems^{1,2}.]

(2) SCREENING TESTS. Twenty-three inhibitor "systems" including various combinations of sodium nitrite and inhibitors listed in Table VII were screened in a simulated water brake environment. Table VIII presents the inhibitor "systems" investigated and the local-action corrosion rates determined for each. The corrosion rates were measured utilizing the polarization resistance technique. Based on these results, the following inhibitor systems were selected for further study:

- (a) Nalco 439
- (b) Sodium Nitrite and Emulsifier STH
- (c) Calgon CS

(3) FURTHER STUDY. Simulated exposure tests conducted to characterize crevice corrosion susceptibility determined that both Nalco 439 and Calgon CS do not inhibit corrosion in tight crevices (Figures 14 & 15). NAVAIRENGCEN previously determined this behavior to be characteristic of sodium nitrite, by itself (Figure 16). On the other hand, the sodium nitrite and Emulsifier STH system effectively eliminated crevice corrosion. Figure 17 shows these results.

Because Nalco 439 and Calgon CS behaved similarly to sodium nitrite in a crevice situation, the same hypothetical model was used to estimate crevice corrosion rates compared to those determined for sodium nitrite. As can be seen from the plot of the polarization and potential data (Figure 18), neither Nalco 439 nor Calgon CS appears to have any advantage over sodium nitrite in a crevice situation. These predictions agree with the results of the exposure tests.

Simulated exposure tests were conducted to generate added data on the sodium nitrite-Emulsifier STH system because of its demonstrated effectiveness in reducing crevice corrosion. Beaker tests were conducted in .2% salinity water @ 180°F under the following inhibitor concentrations:

- (a) Emulsifier STH (.005%) + Sodium Nitrite (.5%)
- (b) Emulsifier STH (.05%) + Sodium Nitrite (.5%)
- (c) Emulsifier STH (.5%) + Sodium Nitrite (.5%)

Crevice corrosion was observed at both lower concentrations of Emulsifier STH after two weeks in test.

[]

However, at a .5% concentration, Emulsifier STH again prevented crevice corrosion after 1 month exposure.

In a simulated water brake solution, Emulsifier STH by itself, initially inhibits corrosion at about the same rate as sodium nitrite. However, in a short period of time (3 days), Emulsifier STH loses much of its inhibiting property and localized corrosion initiates at an increasing rate. Both exposure tests and polarization resistance measurements established this fact. Figure 19 is a plot of corrosion rate versus time for Emulsifier STH initially at .5% in a simulated brake water solution.

The effect of Emulsifier STH addition on bi-metallic corrosion in a nitrite-inhibited system was investigated utilizing techniques similar to those described in B.1.a. Figure 20 shows the effect of Emulsifier STH addition on the corrosion potential of the other alloys in the system. Table IX presents a comparison of the local-action corrosion rates in the nitrite-STH system with those that occur in a solution treated only with sodium nitrite. From the data, it appears that addition of Emulsifier STH neither significantly accelerates corrosion of other alloys in the system nor increases the susceptibility towards bi-metallic corrosion.

3. SUMMARY

a. EFFECT OF PH TREATMENT IN CATAPULT WATER BRAKE SYSTEMS. The results indicate pH treatment will reduce crevice corrosion susceptibility in a nitrite-inhibited water brake system. The pH will have to be adjusted to a level of about 12 before a significant reduction can be effected. At this pH concentration, scaling will occur in the water brake tank. This might be a major constraint.

Whether pH treatment is justified as a means of reducing crevice corrosion susceptibility in a nitrite-inhibited water brake system depends, in part, on the results of the shipboard evaluation phase. Previous research has shown that even though crevice corrosion occurs in the presence of the sodium nitrite inhibitor, it occurs at a substantially lower rate than without the inhibitor. If significant crevice corrosion is not documented during the shipboard evaluation, pH treatment will not be justified.

b. STRESS CORROSION CRACKING SUSCEPTIBILITY. The two steel alloys presently specified in the fleet for fabrication of water brake cylinders are susceptible to stress corrosion cracking in the typical brake water environment (.2% salinity water @ 180°F). Addition of sodium nitrite will eliminate stress corrosion susceptibility for one alloy (MPR-12) but has no beneficial effect on the other alloy (SAE 4340). Sodium nitrate or ethylene glycol present

In the water brake system will not increase the tendency of either alloy towards stress corrosion. Ph treatment, also, will not adversely affect either steel alloy. The alloy specified in NAEC MPR-12 is significantly less susceptible to stress corrosion than the SAE 4340 alloy originally specified. The MPR-12 alloy is a stronger and more ductile alloy possessing superior fracture toughness.

c. OPTIMIZATION OF INHIBITOR TREATMENT.

Sodium nitrite still appears to be the optimum inhibitor for control of corrosion in catapult water brake systems. Both Calgon CS and Nalco 439 reduce corrosion to the same order of magnitude as sodium nitrite, however, both systems are significantly more expensive (Table X). Neither Calgon CS nor Nalco 439 shows a significant advantage over sodium nitrite in preventing corrosion in tight crevices.

Emulsifier STH combined with sodium nitrite did prove to be advantageous in reducing crevice corrosion. By itself, Emulsifier STH was not comparable to the sodium nitrite inhibitor for it exhibited limited ability to prevent corrosion after an extremely short period of time (Figure 19). The wetting agent property of Emulsifier STH may cause the observed reduction in crevice corrosion when used with sodium nitrite. The increased cost of adding a wetting agent to the water brake system in order to reduce crevice corrosion remains to be justified. Addition of Emulsifier STH to a water brake system to reduce crevice corrosion would triple the cost of inhibitor treatment (Table X). The results of the shipboard evaluation will supply the necessary information by documenting the frequency and rate of crevice corrosion that can be anticipated in an operating water brake system.

C. SHIPBOARD EVALUATION OF SODIUM NITRITE INHIBITOR

1. EXPERIMENTAL PROCEDURES. The shipboard evaluation of the sodium nitrite inhibitor was designed to determine the rate at which corrosion occurs in two separate operational water brake systems - one with inhibitor treatment and one without inhibitor treatment. For the evaluation, NAVAIRENGCEN selected the water brake systems for the aft catapults (Nos. 3 and 4) on the aircraft carrier USS Constellation (CVA-64). In the past, the water brake systems for the aft catapults have exhibited the most deterioration due to corrosion.

For the study, as many new, uncorroded components as practical were installed in the water brake systems. Both the water brake cylinders and catapult pistons were new. The water brake cylinders were fabricated from SAE 4340 steel.

A team from NAVAIRENGCEN installed an automatic corrosion-rate monitoring instrument onboard ship during the week of August 21, 1972. Figures 21 thru 25 show the installation. The corrosion rate measuring instrument receives electrical signals from four sensing probes, two probes installed in each water brake system. The meter automatically converts the electrical signals to a direct reading of corrosion rate (mpy). The instrument is equipped with a strip recorder that permanently records data via a channel scanning sequence. It was anticipated that the data supplied by the instrument would help to evaluate the effectiveness of inhibitor treatment in the water brake system.

The particular instrument model installed on ship is a Petrolite Model 1004. The instrument measures electrochemical polarization resistance and is specifically calibrated for mils per year rate of metal loss at sensitivities of 0-1 to 0-1000 mpy in 10 ranges. The instrument features a unique nulling and zero offsetting circuit which provides reproducible polarization measurements. Studies conducted previously by NAVAIRENGCEN indicated this type of instrument would be effective in monitoring inhibitor performance.

At the start of the evaluation, about 500 pounds of sodium nitrite were added to the No. 3 water brake system giving an approximate concentration of 1.25%, by weight. Also, water samples were taken from each system for detailed chemical analysis. Chemical analysis of the water samples characterized initial conditions and identified possible corrodents. The NAVAIRENGCEN team held a briefing with the ship's V-2 Division to instruct responsible personnel on data acquisition required during the course of the evaluation. Data acquisition by ship's personnel included chloride measurements on water samples from both brake tanks and sodium nitrite measurements on water samples taken from Tank No. 3. Also, 1-gallon samples of brake water were taken monthly and shipped back for laboratory measurements. After about 1 year of operation, a NAVAIRENGCEN inspection team was scheduled to compare the extent of corrosion between the No. 3 catapult components and the No. 4 catapult components.

2. RESULTS

a. SHIPBOARD INSPECTION, BRAKE WATER ANALYSES AND MEASUREMENTS. Operational evaluation of the sodium nitrite corrosion inhibitor was conducted initially over a 15-month period (August, 1972 thru November, 1973). It proved to be unsatisfactory. Significant corrosion occurred in the No. 3 water brake system which had been treated with the sodium nitrite inhibitor. Inhibitor treatment of the system, however, was not accomplished as had been planned.

The concentration of inhibitor in the brake water was allowed to decrease below the minimum recommended level for a significant period of time. Also, the salinity of the brake water exceeded the recommended maximum level (.2%) at different times.

Table IX summarizes the results of the chemical analyses of water samples taken initially from the two water brake tanks. The results reflect data compiled by three independent laboratories^{13, 14, 15}. Chlorides were present at significant concentrations in both tanks. Previous research documented chloride contamination in the brake water as the primary cause of accelerated corrosion throughout the system. However, according to previous information, it was believed that chloride contamination rarely exceeded a level of $\approx .1\%$ (.2% salinity). The water analyses show that chlorides are present in significantly greater concentrations, as high as .3%. Consequently, it was expected that corrosion would occur at higher rates than had been predicted from laboratory measurements. The laboratory data had been gathered under a maximum salinity of .2%. Except for sodium nitrite which was added to the No. 3 water brake, the initial data does not reflect the presence of any other chemical constituents in sufficient quantity to significantly effect corrosion of water brake hardware.

Table XII shows the chemical analyses of brake water samples sent back from the ship during the course of the evaluation. As is evident, the concentration of the sodium nitrite dropped below the recommended minimum (.75%) after only 1 month. Thereafter, the inhibitor level was never above the minimum recommended concentration required for effective corrosion inhibition. The relative benefits of inhibitor treatment, therefore, could not be meaningfully evaluated.

Shipboard evaluation procedures specified controlling sodium nitrite concentration to a minimum of .5%, by weight, in the No. 3 brake tank; however, Table XII shows it was not done. This was due to a lack of sufficient inhibitor onboard the ship to replenish the system. The rate of inhibitor depletion was determined to be more a function of draining and skimming required to rid the water of oil and contamination than a function of a chemical conversion reaction.

The water analyses do indicate that even though the inhibitor concentration had dropped below the minimum recommended level, there was some benefit. For example, at 2 months, the salinity of the brake water increased to a very high level (.65%). With the inhibitor present at .45%, the corrosivity of the water was only .70 mpy to steel. The uninhibited brake water, on the other hand, with a salinity of only .16% was corroding steel at 6.4 mpy.

The overwhelming evidence from laboratory investigations still suggested that inhibitor treatment properly effected would substantially reduce corrosion of the catapult water brake systems. Therefore, it was decided to extend the shipboard evaluation of the sodium nitrite inhibitor with some modification of treatment procedures in order to circumvent the difficulties encountered over the previous 15 months.

The second operational evaluation of the sodium nitrite inhibitor lasted for about 12 months (January, 1974 to January, 1975). This time the results proved to be dramatically different. Inspection of water brake components showed that the No. 3 water brake experienced only minimal corrosion whereas the No. 4 water brake had corroded extensively (average pit depth $\approx$ 20 mils). Figures 26 thru 30 show some of the hardware removed from the water brakes after the 12 month evaluation period. The beneficial effects are strikingly apparent. Figure 30 shows the striker ring removed from the No. 1 water brake. The exact length of time it was in service is unknown, however it is obvious that failure was imminent. The more recent results of the shipboard inhibitor evaluation demonstrate positively that deterioration due to corrosion such as occurred on the striker ring can essentially be eliminated.

Table XIII presents data gathered on water samples returned periodically from the ship during the second evaluation study. The data indicates that only once during the course of the evaluation did the inhibitor concentration drop appreciably below .5%. The difference in corrosion rate measured on steel probes @ 180°F correlates excellently with what was observed during the final inspection. On the average, corrosion in the uninhibited brake water occurs at approximately 100 X the rate of corrosion in the inhibited brake water.

b. PERFORMANCE OF CORROSION RATE MONITORING INSTRUMENT. Over the course of the initial 15-month evaluation onboard ship, the performance of the automatic corrosion rate measuring instrument was erratic. Several factors contributed to this erratic performance. Initially, the scale sensitivities set up on the four data channels were too high and the meter was driven off scale. The initial scale sensitivity settings were based on data obtained under simulated laboratory conditions, but as mentioned, actual shipboard operating conditions caused higher corrosion rates than had been anticipated. The scale settings had to be changed to properly measure the data input signals.

Another problem causing less than optimum data acquisition from the instrument was poor pen performance.

This was due to improper maintenance of the recording pens and possibly due to abnormally severe environmental conditions in the compartment where the instrument was first located. The data acquisition procedures were modified in an attempt to reduce pen maintenance requirements. Use of the event marking pen was discontinued. Thus, only one recording pen was required. A constant signal meter prover was plugged into channel No. 4 to indicate channel sequence, in the absence of the event marking pen. This eliminated data acquisition from one of the sensing probes. Improved reliability justified the reduction in data output.

At first, a malfunction in the automatic potential null circuit of the instrument was also suspected. Potential differences greater than 100 MV were recorded between the steel sensing electrodes. Ordinarily, a potential difference greater than 100MV between two electrodes of the same alloy in the same environment would not be expected. However, past laboratory data indicated that in inhibited nitrite water contaminated with chlorides, potential variations greater than 100 MV can and do occur. This phenomena is directly related to the activation and repassivation of the steel surface. At local spots on the surface, the protective oxide film formed by the addition of the nitrite inhibitor often breaks down. Repassivation takes place at the localized breaks in the film if inhibitor is present in sufficient concentration. Variations in potential are indicative of this type of behavior. Consideration of this phenomena indicated the potential null circuit was operating satisfactorily.

About four months into the program, relays in the multiplexing stage of the instrument failed. The reason for the failure of the relays is unknown. The instrument was repaired while the ship was in Subic Bay at about six months into the program. Because of the problems encountered up to that time, NAVAIRENGCEN decided to forestall further use of the instrument until it could be checked out thoroughly by representatives of NAVAIRENGCEN when the ship returned to San Diego.

Upon return to San Diego, the instrument was determined to be operating perfectly. For the second evaluation study, it was decided to install the instrument in another compartment where the operating environment was less severe. The instrument was relocated and set in operating condition. Before the ship's departure, NAVAIRENGCEN personnel checked operation of the instrument and determined everything to be functioning properly. During the second evaluation study, however, data acquisition proved to be just as erratic. The exact cause of the problem was never determined.

For the pilot evaluation program, the Petrolite Model 1004 corrosion rate instrument seemed to be the most desirable. It is a sophisticated piece of instrumentation that affords excellent flexibility and capability in gathering data required for an evaluation-type program. The problems encountered, however, indicate that a less sophisticated, more rugged instrument would be required if it were to be used on a fleet-wide basis.

3. SUMMARY. Shipboard evaluation of the sodium nitrite inhibitor confirms the results of the laboratory studies. If the concentration of sodium nitrite is maintained at a proper level, corrosion of the catapult water brakes will be essentially eliminated. There was some evidence of crevice corrosion (striker ring/annulus ring) however it was minimal, far less than occurred in the absence of the inhibitor. Additional treatment of the brake water other than sodium nitrite addition does not appear justified.

In order to maintain the concentration of sodium nitrite above the minimum specified during the shipboard evaluation ($\approx .5\%$), V-2 Division personnel estimate it required approximately 100 lbs/week during normal carrier operations. On this basis, to treat all four water brake systems, approximately 1600 lbs. of sodium nitrite would be required per month. The material cost would be about \$300/month or \$3600/yr. Over a 5 to 10 year period, this cost would be insignificant compared to the replacement costs of water brake hardware.

Because of the bulk quantity required, storage of the sodium nitrite is somewhat cumbersome. Procedures for optimum procurement, containment, and storage of the sodium nitrite inhibitor need to be further investigated. Also, the environmental implications of using sodium nitrite to treat water brake systems throughout the fleet need to be assessed.

It is possible that the estimated quantities of inhibitor required are overly conservative. During the shipboard evaluation, it was specified that the concentration of sodium nitrite be maintained above $.5\%$ after an initial dosage to approximately 1.25% . The $.5\%$ minimum specification was based on laboratory data which indicated that at $.2\%$ salinity, $.5\%$ sodium nitrite was necessary to prevent pitting. Data was gathered at $.2\%$ salinity because that is the maximum permissible salinity level of the brake water before dumping is required. Analysis of the brake water samples obtained during the last evaluation (Table XIII) show that the salinity seldom approached $.2\%$. The No. 3 and No. 4 water brakes were selected because historically they have exhibited the highest salinity.

It appears based on the water sample data that the minimum concentration of sodium nitrite necessary to prevent pitting might be lower than the .5% level specified during the shipboard study. If so, the net amount of sodium nitrite necessary to control corrosion in all four water brakes might be significantly less than required for this initial shipboard study. Additional laboratory studies should be conducted to determine the minimum concentration of sodium nitrite necessary to prevent pitting as a function of salinity.

The results of the inhibitor study overwhelmingly favor expansion of the program designed ultimately to accomplish fleetwide inhibitor treatment of the catapult water brake systems. Laboratory studies showed that inhibitor treatment will eliminate stress corrosion susceptibility of the steel now specified for water brake cylinders. This means an increase in safety and system reliability. The shipboard evaluation confirmed what the laboratory studies had predicted - that proper inhibitor treatment would reduce general corrosion to almost zero. The potential savings in maintenance costs are inestimable at this time but just a cursory analysis would seem to indicate the savings will be sizeable.

D. CONCLUSIONS

1. Shipboard evaluation of the sodium nitrite inhibitor confirms the results of the laboratory studies. Sodium nitrite added to the water brake tanks @ 1.25%, by weight, will virtually eliminate corrosion.
2. Sodium nitrite inhibitor treatment of the catapult water brakes will improve safety and increase system reliability. It will also significantly reduce maintenance costs.
3. Of the inhibitors tested, sodium nitrite is the optimum corrosion inhibitor for controlling corrosion of steel hardware in catapult water brakes.
4. Both steel alloys now being used for water brake cylinders are susceptible to stress corrosion cracking in the typical water brake environment (.2% salinity water @ 180°F).
5. The steel alloy now specified for water brake cylinders (NAEC-MPR-12) possess approximately 1 1/2 times the fracture toughness of the steel alloy formerly specified in MPR-12.
6. Sodium nitrite inhibitor treatment will eliminate the stress corrosion cracking susceptibility of the alloy now specified in MPR-12. Sodium nitrite inhibitor

treatment will not eliminate the stress corrosion cracking susceptibility of the alloy previously specified.

7. Crevice corrosion susceptibility in the presence of the sodium nitrite inhibitor can be reduced by either pH treatment or the addition of another inhibitor (Emulsifier STH). Ph treatment will not increase bi-metallic corrosion or stress corrosion susceptibility, however it will cause scale formation above a level of pH = 10. Loose scale flaking off could clog pump strainers.

8. Crevice corrosion did occur in the inhibited water brake during the shipboard evaluation however it was minimal and does not justify additional inhibitor treatment. Sodium nitrite, by itself, provides adequate control of crevice corrosion.

9. Emulsifier STH in combination with sodium nitrite eliminates crevice corrosion even in tight crevices. None of the other inhibitors tested including sodium nitrite, by itself, were able to eliminate crevice corrosion. The nitrite - STH combination might be advantageous in other applications.

10. The concentration of sodium nitrite required to adequately control corrosion in operating water brakes might be lower than the concentration determined from laboratory studies. Laboratory data was gathered in .2% salinity water. During the second shipboard evaluation, the brake water seldom approached .2% salinity.

11. Optimum procedures for procurement, containment, and storage of the sodium nitrite need to be determined.

12. The environmental implications of using sodium nitrite on a fleetwide basis need to be assessed.

13. The results of the program overwhelmingly favor expansion of the program to initiate treatment of catapult water brakes on other ships. Additional evaluation studies under controlled conditions are required prior to initiating inhibitor treatment on a fleetwide basis.

E. RECOMMENDATIONS

1. Expand the catapult water brake inhibitor program to include evaluation studies on other ships.

2. Assess the environmental implications of using the sodium nitrite inhibitor on a fleetwide basis.

3. Determine optimum procedures for procurement, containment, and storage of sodium nitrite in the quantities that will be required for water brake treatment.

4. Determine under simulated laboratory conditions the minimum concentration of sodium nitrite required to prevent pitting for a range of salinities.

5. Investigate the feasibility of using a corrosion inhibitor combination similar to the sodium nitrite - Emulsifier STH combination as an additive in the flight deck washdown solution to help control flight deck corrosion.

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TABLE 1
OTHER ALLOYS IN WATER BRAKE SYSTEM

<u>IDENTIFICATION NO.</u>	<u>DESCRIPTION</u>
1.	Cast Bronze, QQ-C-390 Alloy D3
2.	Cast Bronze, QQ-C-390 Alloy B5
3.	Copper, electrolytic tough pitch, QQ-C-502
4.	Copper-nickel-aluminum, QQ-N-286 CL.A., Form 2, cold drawn and age hardened
5.	Copper-nickel, QQ-N-281 CL.A, Form 1, cold drawn
6.	Brass, QQ-B-637
7.	Phosphor bronze, QQ-B-750 cond. A. Hard
8.	Tin bronze, MIL-B-16261 Grade III
9.	Tin bronze, MIL-M-16576

TABLE II

TYPICAL PROPERTIES OF SAE 4340 ALLOY
STEEL SPECIFIED FOR WATER BRAKE CYLINDERS

Tensile strength, psi -	185,000
Yield strength, psi -	175,000
Percent elongation in 2 in. -	6
Hardness -	R _C 36
Heat treatment -	Quench and Temper

TABLE III

MINIMUM MECHANICAL PROPERTIES OF THE
STEEL ALLOY SPECIFIED IN NAEC-MPR-12

Tensile strength, psi -	175,000
Yield strength, psi -	160,000
Percent Elongation in 2 in. -	12
Hardness -	R _c 36
Heat treatment -	Quench and Temper

TABLE IV

EFFECT OF pH TREATMENT ON LOCAL ACTION
CORROSION RATE WITHIN A CREVICE OF SAE 4340 STEEL
180°F, .2% SALINITY, O₂ DEPLETED

<u>pH</u>	<u>CORROSION RATE, MPY</u>
8	1.34
10	.24
12	.19

TABLE V

CORROSION RATE OF COPPER BEARING ALLOYS IN
.2% SALINITY WATER AT 180°F AS A FUNCTION OF PH

<u>ALLOY*</u>	<u>CORROSION RATE, MPY</u>		
	<u>pH=8</u>	<u>pH=10</u>	<u>pH=12</u>
1	.500	.720	1.370
2	.500	.216	1.020
3	.950	.216	.324
4	.020	.011	.014
5	.010	.011	.025
6	.370	.180	1.030
7	.190	.216	.395
8	.360	.115	.502
9	.220	.152	.545

* See Table I

TABLE VI

Stress intensity factors for SAE 4340 and MPR 12 alloy steels in simulated brake water environments.

EXPOSURE CONDITIONS		SAE 4340 Mean $K_{I\sigma}$'s ksi [in] ³	NAEC MPR 12 Mean $K_{I\sigma}$'s ksi [in] ³
1.	Air, 80°F., 50% R.H.	90	121
2.	Water, 180°F., .2% Salinity, no pH treatment	75	111
3.	Water, 180°F., .2% Salinity, 1.25% Sodium Nitrite, no pH treatment	71	120
4.	Water, 180°F., .2% Salinity, 1.25% Sodium Nitrite, pH 12	72	114
5.	Water, 180°F., .2% Salinity, 1.25% Sodium Nitrate, no pH treatment	73	112
6.	Water, 180°F., .2% Salinity, 1.25% Sodium Nitrate, pH 12	70	128
7.	Water, 180°F., .2% Salinity, Ethylene Glycol, no pH treatment	77	124

TABLE VII

SUMMARY OF INHIBITORS SELECTED FOR SCREENING

<u>Inhibitor</u>	<u>Supplier</u>
1. Sodium Nitrite	Chemical Supplier
2. Nalco 439	Nalco Chem. Co. Chicago, Ill.
3. Emulsifier STH	GAF Corporation New York, N.Y.
4. Calgon CS	Calgon Corporation Pittsburgh, Pa.
5. Polyrad 1100A	Hercules, Inc. Wilmington, Del.
6. Dearborn 561	Dearborn Chem. Co. Chicago, Ill.
7. Drewgard 100	Drew Chem. Co. Parsippany, N.J.
8. Sodium Molybdate	Chemical Supplier
9. Betz Corr Shield K7	Betz Laboratories, Inc. Trevose, Pa.
10. Sodium Benzoate	Chemical Supplier
11. Maleic Hydrazide	Chemical Supplier
12. Ferric EDTA	Chemical Supplier
13. Sodium Hexametaphosphate	Chemical Supplier
14. Sodium Phosphate	Chemical Supplier

TABLE VIII

CORROSION RATES DETERMINED FOR CANDIDATE
INHIBITOR "SYSTEMS" IN .2% SALINITY WATER @ 180°F

	<u>Inhibitor</u>	<u>Concentration, %</u>	<u>Rate, MPY</u>
1.	Sodium Nitrite	0.50	0.083
2.	Nalco 439	0.50	0.067
3.	Sodium Nitrite Emulsifier STH	0.25 0.25	0.074
4.	Sodium Nitrite Emulsifier STH	0.25 0.50	0.119
5.	Calgon CS	0.50	0.074
6.	Calgon CS	0.25	0.119
7.	Sodium Nitrite Polyrad 1100A	0.25 0.25	0.119
8.	Sodium Nitrite Sodium Phosphate	0.25 0.25	0.163
9.	Sodium Nitrite Sodium Hexametaphosphate	0.25 0.25	0.163
10.	Dearborn 561	0.50	0.283
11.	Sodium Nitrite Sodium Molybdate	0.25 0.25	0.297
12.	Drewgard 100	0.25	0.357
13.	Drewgard 100	0.50	0.863
14.	Betz Corr Shield K7	0.50	0.450
15.	Betz Corr Shield K7	0.25	1.48
16.	Sodium Nitrite Sodium Benzoate	0.25 0.25	0.875
17.	Ferric EDTA	0.25	1.13
18.	Sodium Phosphate	0.50	2.11
19.	Sodium Molybdate	0.50	4.70

TABLE VIII (cont'd.)

20.	Sodium Hexametaphosphate	0.50	>25
21.	Maleic Hydrazide	0.50	>25
22.	Sodium Benzoate	0.50	>25
23.	Sodium Benzoate	0.25	>25

TABLE IX

CORROSION RATE OF COPPER BEARING ALLOYS IN AERATED,
.2% SALINITY WATER AT 180°F WITH DIFFERENT INHIBITORS

<u>ALLOY*</u>	<u>SODIUM NITRITE 0.5%, BY WEIGHT</u>	<u>SODIUM NITRITE & EMULSIFIER STH 0.25% & 0.25%, BY WEIGHT</u>
1	.446	.320
2	.538	.263
3	.043	.303
4	.092	.079
5	.126	.064
6	.474	.374
7	.720	.434
8	.345	.396
9	.606	.389

* See Table I

TABLE X
COMPARATIVE MATERIAL COST OF INHIBITING ONE
WATER BRAKE TANK OF 5000 GAL. CAPACITY
AT 1.25% INHIBITOR CONCENTRATION (500 lbs.)

<u>Inhibitor</u>	<u>Container</u>	<u>Form</u>	<u>Price/Pound</u>	<u>Material Cost</u>
1. Emulsifier STH Sodium Nitrite (1:1 mix)	425 lb. drum 400 lb. drum	Liquid Solid	\$1.13 .19	\$329.
2. Calgon CS	100 lb. drum	Solid	.60	\$300.
3. Nalco 439	550 lb. drum	Liquid	.51	\$255.
4. Sodium Nitrite (USP grade)	400 lb. drum	Solid	.19	\$ 95.

TABLE XI
SUMMARY OF CHEMICAL ANALYSES OF
WATER SAMPLED INITIALLY FROM CATAPULT
BRAKE TANKS NO. 3 & 4

<u>CONSTITUENT</u>	<u>TANK NO. 3</u> <u>(Inhibited)</u>	<u>TANK NO. 4</u> <u>(Not Inhibited)</u>
Alkalinity, ppm	25	5
Aluminum, ppm	1.2	.3
Calcium & Magnesium, ppm	266	95
Carbonate, ppm	42	8
Chloride, ppm	3370	1310
Copper, ppm	0	0
Total dissolved solids, ppm*	13,215	3044
Fixed dissolved solids, ppm**	10,517	2465
Grease & Oil, ppm	97	21
Hydroxide, ppm	0	0
Total hardness, ppm as CaCO ₃	1025	550
Hydrogen Sulfide, ppm	10.7	1.6
Iron, ppm	.18	.1

TABLE XI (cont'd.)

Nickel, ppm	0	0
Nitrate, ppm	4.3	1.2
Nitrite, ppm	9600	0
pH	7.7	7.3
Resistivity, ohm-cm	85	280
Specific conductance, ohm/cm	17,000	4650
Sulfate, ppm	654	402
Sulfite, ppm	0	5.8
Zinc, ppm	0	0

* The dried residue from evaporation of the filtrate after separation of suspended solid.

** The residue remaining after ignition of the dissolved solids collected by evaporating the filtrate.

TABLE XII - ANALYSES OF BRAKE WATER SAMPLES (1st Evaluation)

TANK NO. 3

Date	pH	% Salinity*	Resistivity (Ω -cm)	% NaNO ₂	Corrosivity, mpy
Initial	8.1	.187	85	1.44	.70
1 mo.	8.0	.556	85	.90	1.50
2 mo.	7.5	.649	120	.45	.70
3 mo.	7.6	.262	180	.25	1.50
4 mo.	8.1	.115	610	.06	.60
5 mo.	7.6	.056	205	.54	.29
6 mo.	7.0	.087	500	0	1.10
7 mo.	7.6	.047	952	0	1.49
8 mo.	8.7	.356	142	.10	.27
9 mo.	7.0	.024	1625	0	2.21

* For reference, the salinity of sea water is 3.5%

TABLE XII (cont'd.)

TANK NO. 4

<u>Date</u>	<u>pH</u>	<u>% Salinity</u>	<u>Resistivity (Ω-cm)</u>	<u>% NaNO₂</u>	<u>Corrosivity, mpy</u>
Initial	7.9	.221	280	0	13.4
1 mo.	7.9	.241	250	0	13.4
2 mo.	7.6	.161	610	0	6.4
3 mo.	7.7	.030	780	0	7.2
4 mo.	8.0	.005	3150	0	.94
5 mo.	6.3	.037	1380	0	1.05
6 mo.	6.9	.077	526	0	1.15
7 mo.	7.7	.0075	3125	0	1.29
8 mo.	8.7	<.0055	3560	0	.60
9 mo.	7.4	<.0055	3240	0	.75

TABLE XIII - ANALYSIS OF BRAKE WATER SAMPLES (2nd Evaluation)

TANK NO. 3					
Date	pH	% Salinity	Resistivity (Ω -cm)	% NaNO ₂	Corrosivity, mpy
Initial	7.3	.2	35	1.9	.29
1 mo.	7.3	.022	60	1.36	.13
2 mo.	7.4	.017	54	1.68	.04
3 mo.	7.7	.060	71	.85	.14
4 mo.	7.3	.038	200	.24	.09
5 mo.	6.7	.005	1000	.03	.07
6 mo.	7.4	.032	167	.32	.03
7 mo.	7.8	.010	169	.26	.15

TABLE XIII (cont'd.)

TANK NO. 4

<u>Date</u>	<u>pH</u>	<u>% Salinity</u>	<u>Resistivity (Ω-cm)</u>	<u>% NaNO₂</u>	<u>Corrosivity, mpy</u>
Initial	5.9	.067	526	0	26.5
1 mo.	7.0	.017	3517	0	16.4
2 mo.	7.5	.020	1667	0	4.69
3 mo.	7.0	.020	1667	0	17.1
4 mo.	7.1	.023	1667	0	17.1
5 mo.	6.6	<.005	33333	0	1.52
6 mo.	6.6	.008	17500	0	8.50
7 mo.	6.4	.005	15200	0	3.07

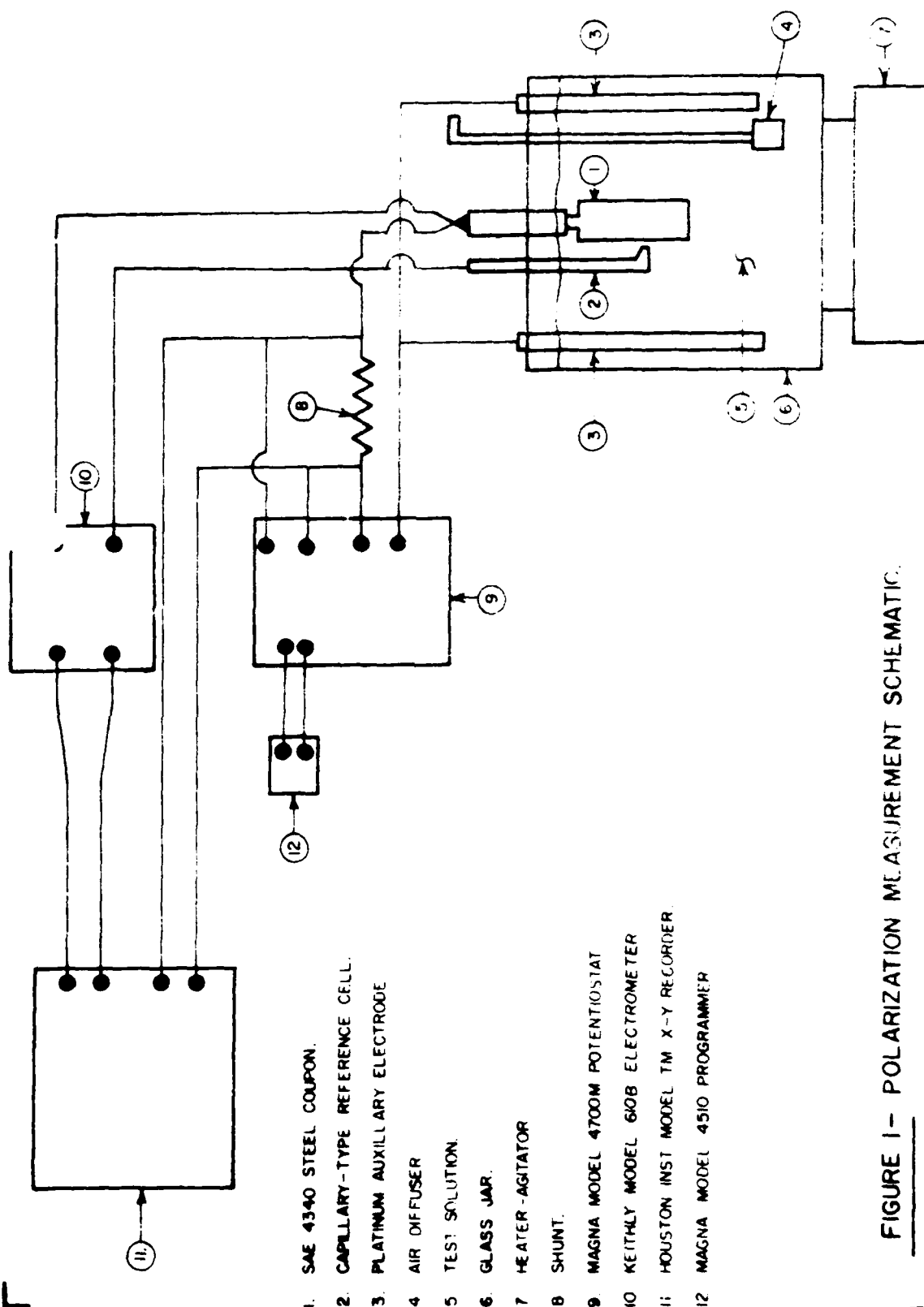


FIGURE 1- POLARIZATION MEASUREMENT SCHEMATIC.

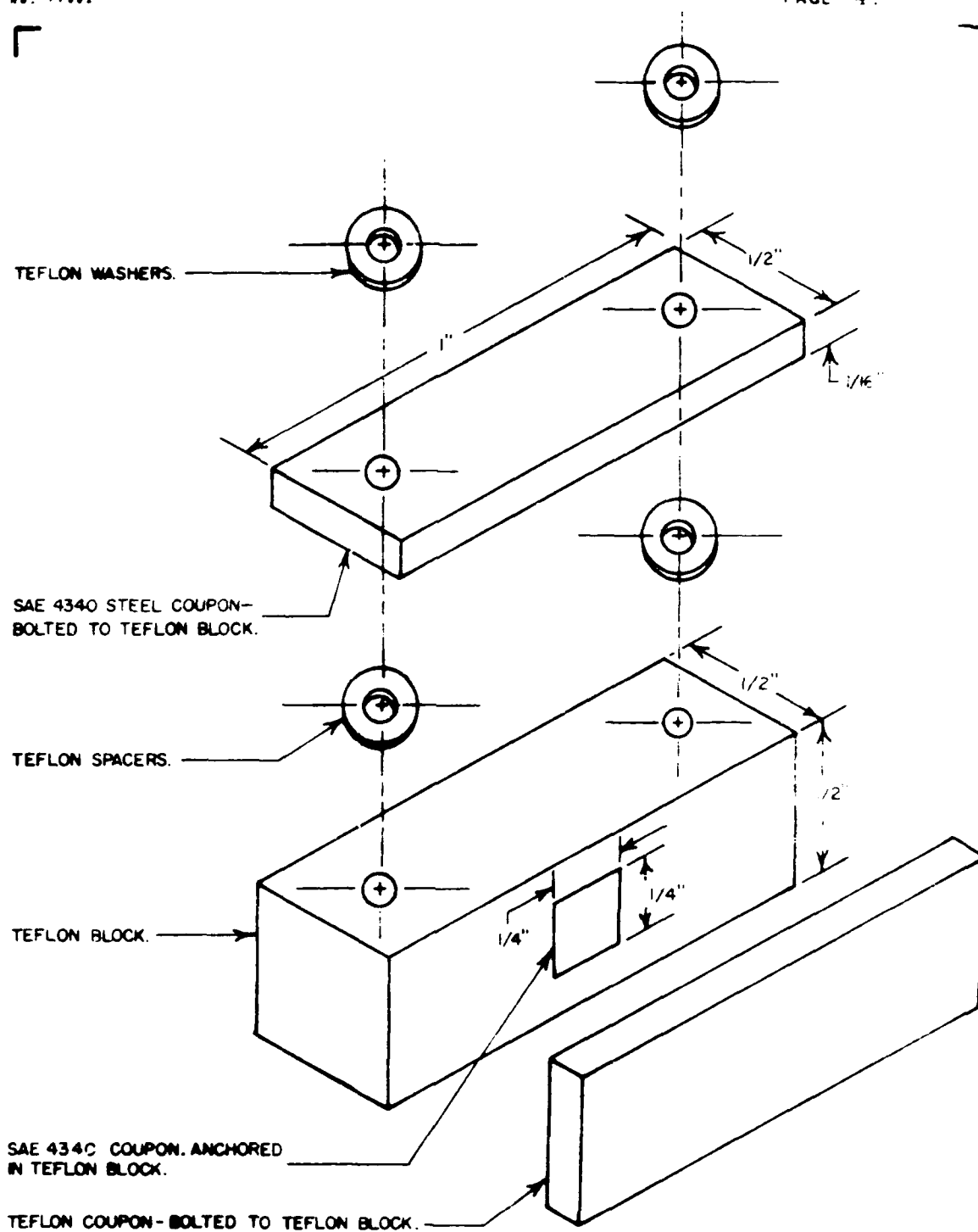


FIGURE 2- CREVICE COUPON ASSEMBLY.

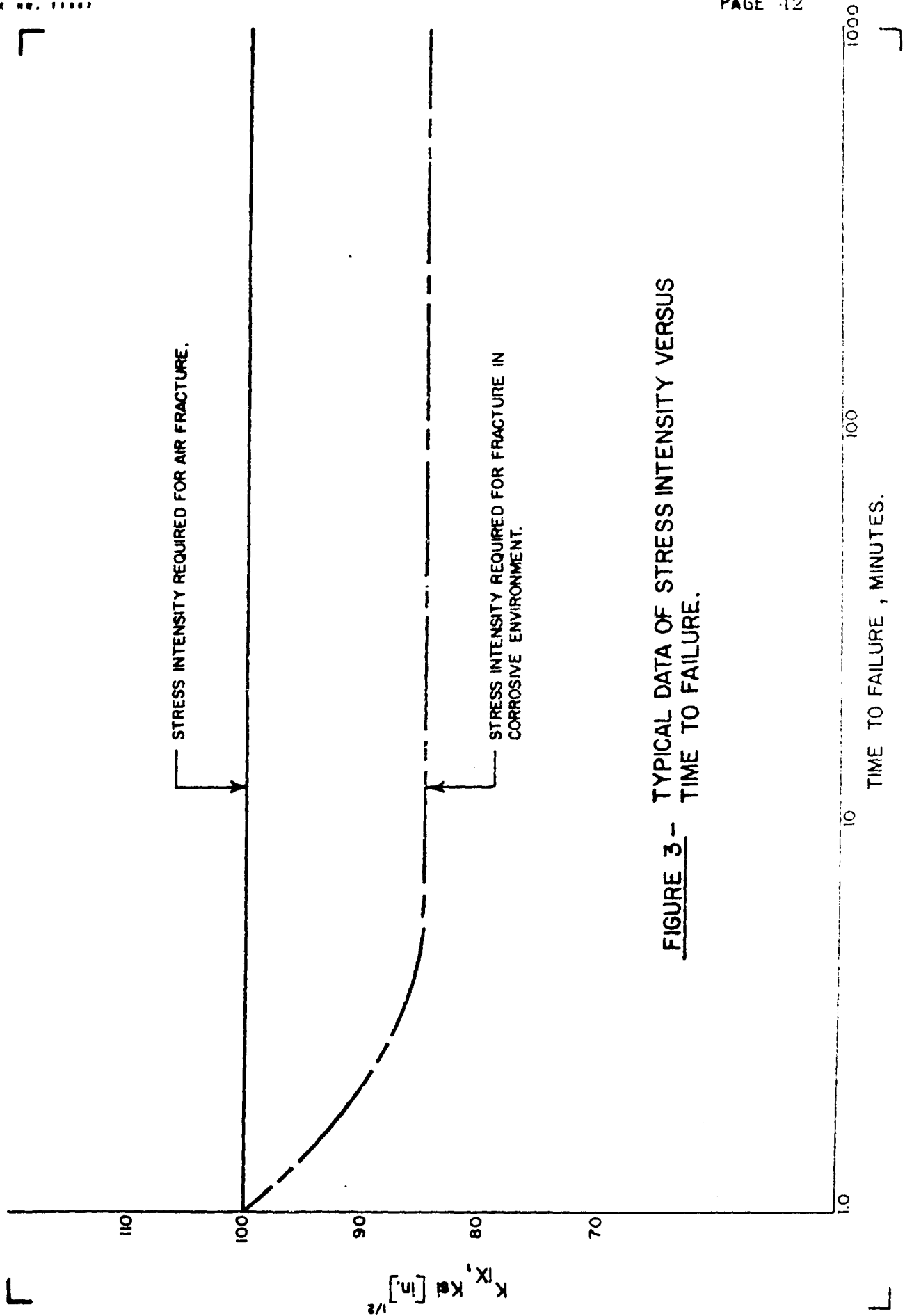


FIGURE 3-- TYPICAL DATA OF STRESS INTENSITY VERSUS TIME TO FAILURE.

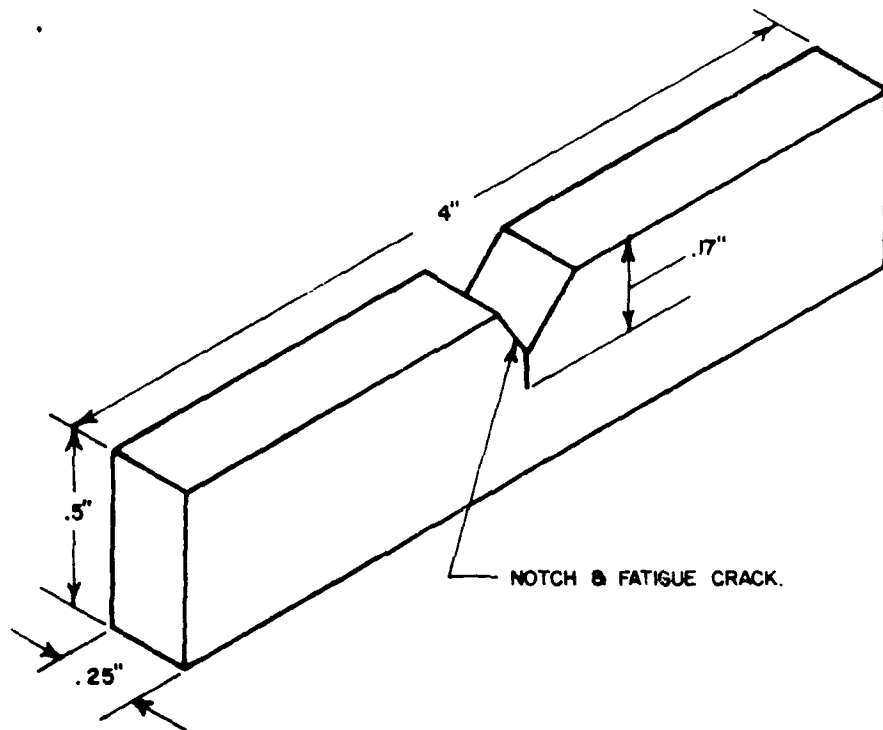


FIGURE 4.— STRESS CORROSION CRACKING TEST SPECIMEN.



FIGURE 5 - GENERAL ARRANGEMENT OF TEST RIG
FOR STRESS CORROSION TESTS

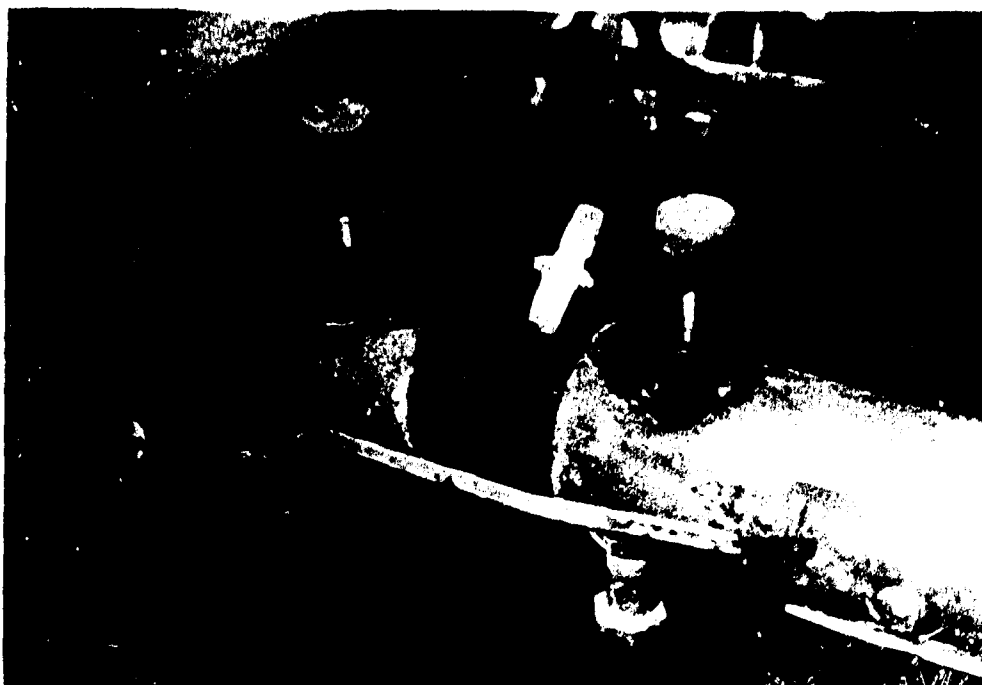


FIGURE 6 - TEST SPECIMEN STRESSED
AS CANTILEVER BEAM



FIGURE 7 - TEST SPECIMEN SURROUNDED BY
FLEXIBLE RESERVOIR CONTAINING
TEST SOLUTION

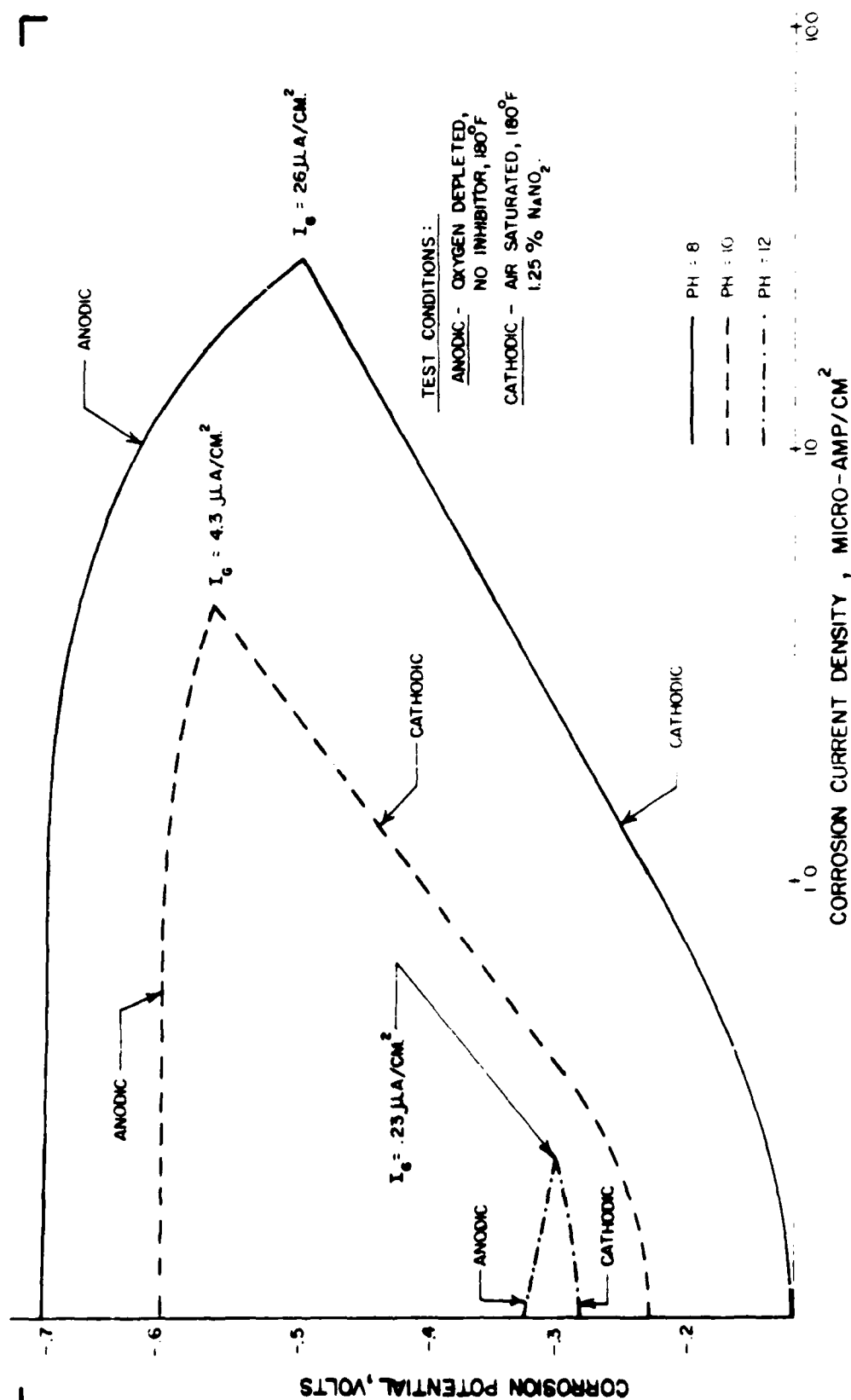


FIGURE 8-- COMPOSITE PLOT OF POLARIZATION DATA FOR SAE 4340 STEEL
IN SIMULATED BRAKE WATER AT VARIOUS PH LEVELS.

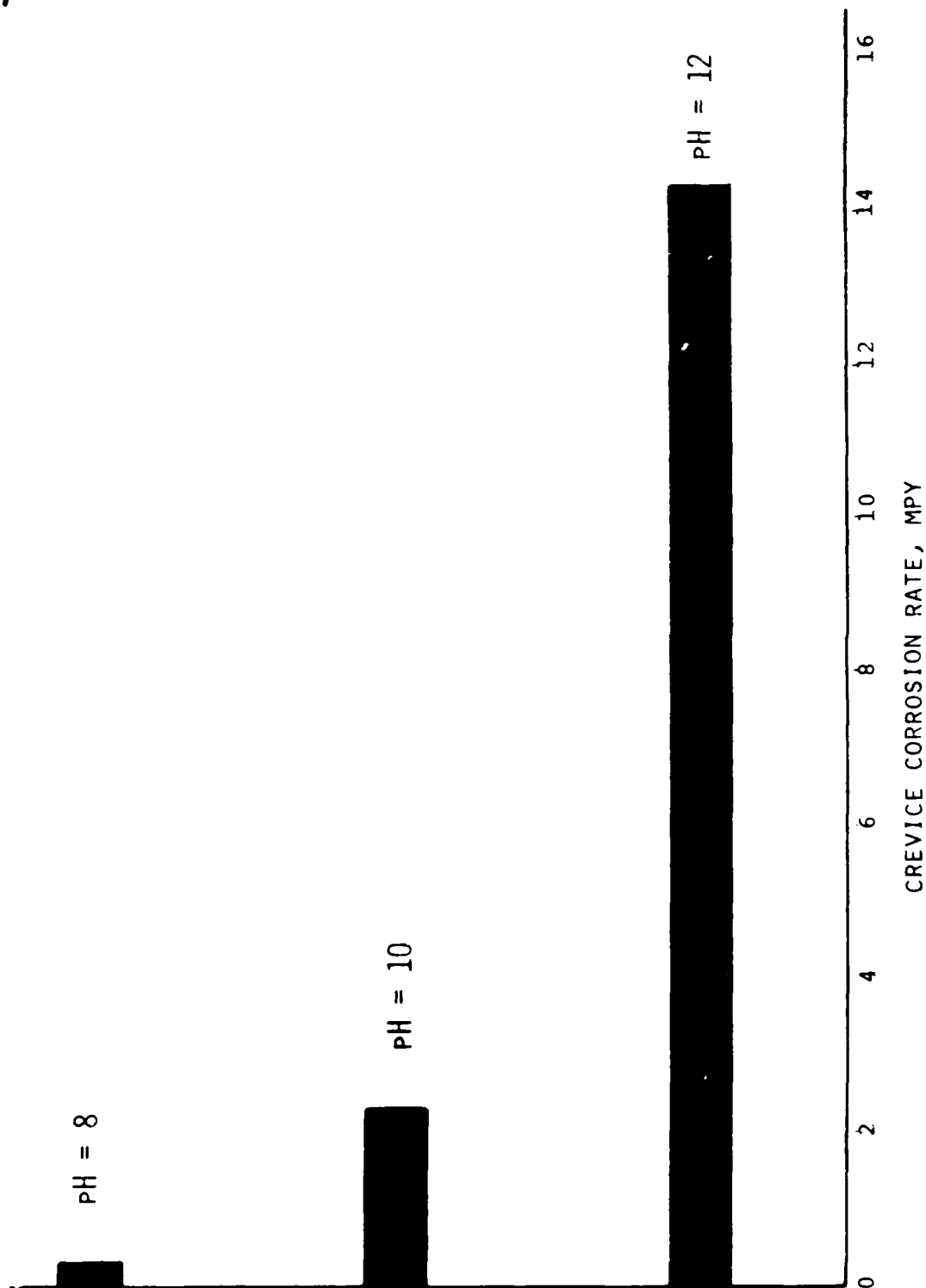


FIGURE 9 - BAR GRAPH SUMMARIZING CREVICE CORROSION RESULTS

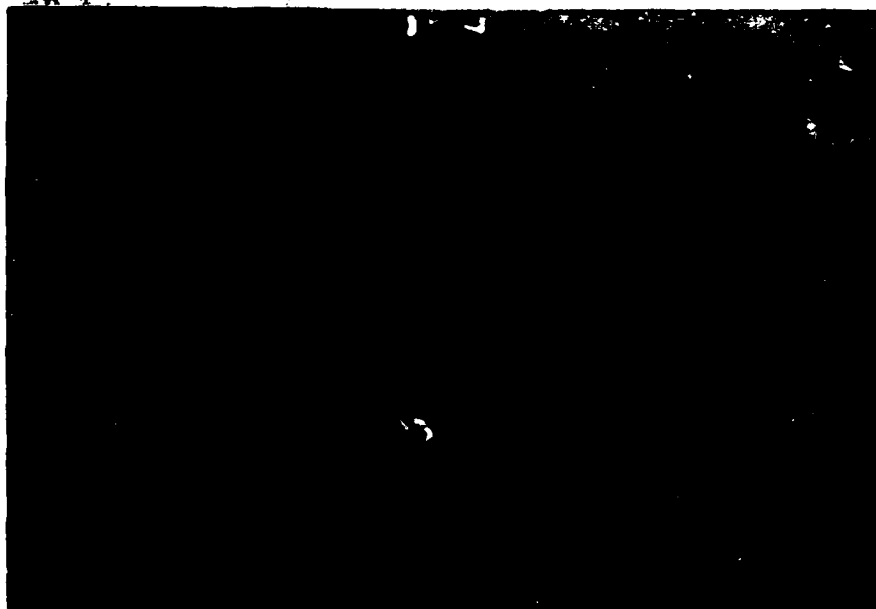


FIGURE 10 - CREVICE COUPON ASSEMBLIES AFTER
3 MONTHS SIMULATED EXPOSURE

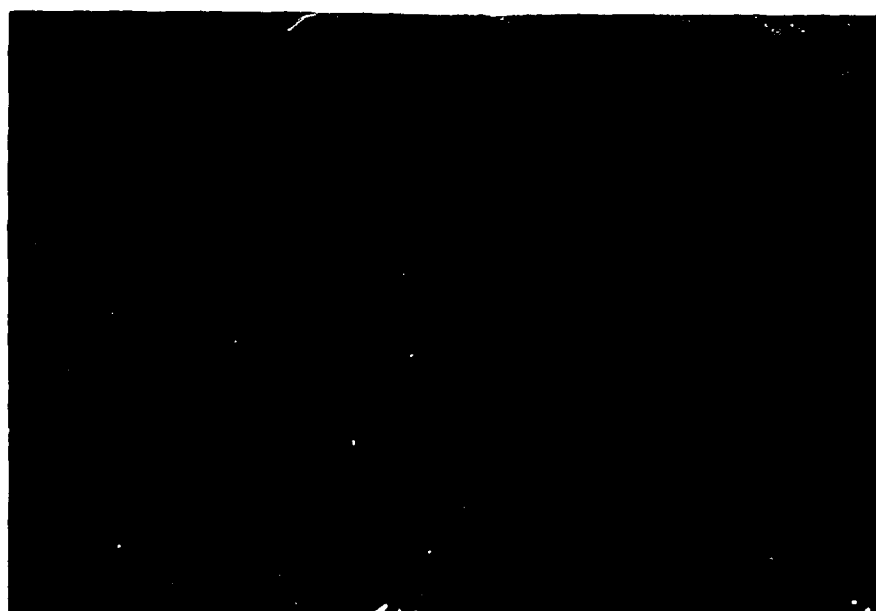


FIGURE 11 - CREVICE COUPON ASSEMBLIES AFTER
3 MONTHS SIMULATED EXPOSURE

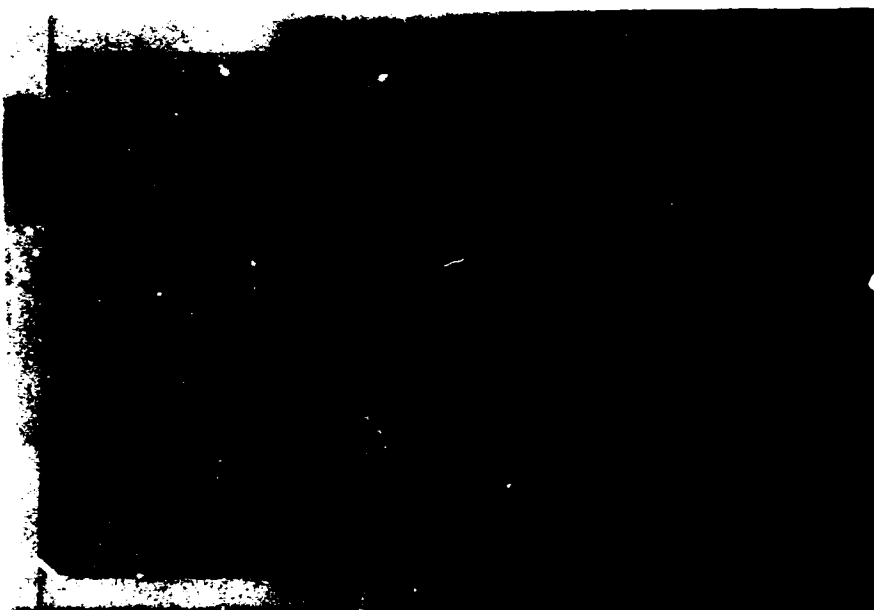


FIGURE 12 - CREVICE COUPON ASSEMBLIES AFTER
3 MONTHS SIMULATED EXPOSURE

NOTE: NUMBERS CORRESPOND TO ALLOYS IDENTIFIED IN TABLE I.

— STEEL —



PH 12

— STEEL —



PH 10

— STEEL —



PH 8

FIGURE 13.- CORROSION POTENTIAL, VOLTS, SHE, 180°F, 0.2% SALINITY, 1.25% NaNO_2 , OXYGEN SATURATED.

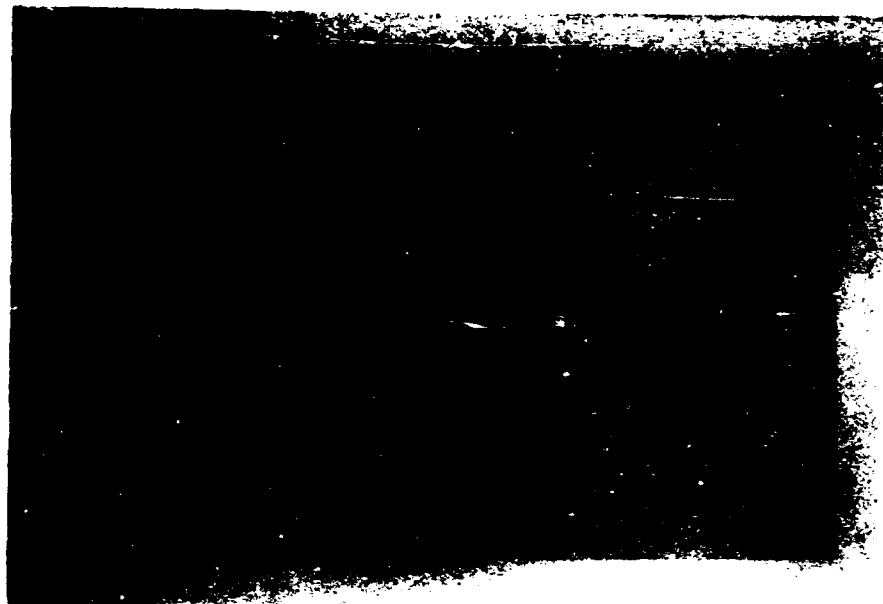


FIGURE 14 - CREVICE COUPON ASSEMBLY, CALGON
CS (1 MONTH EXPOSURE)

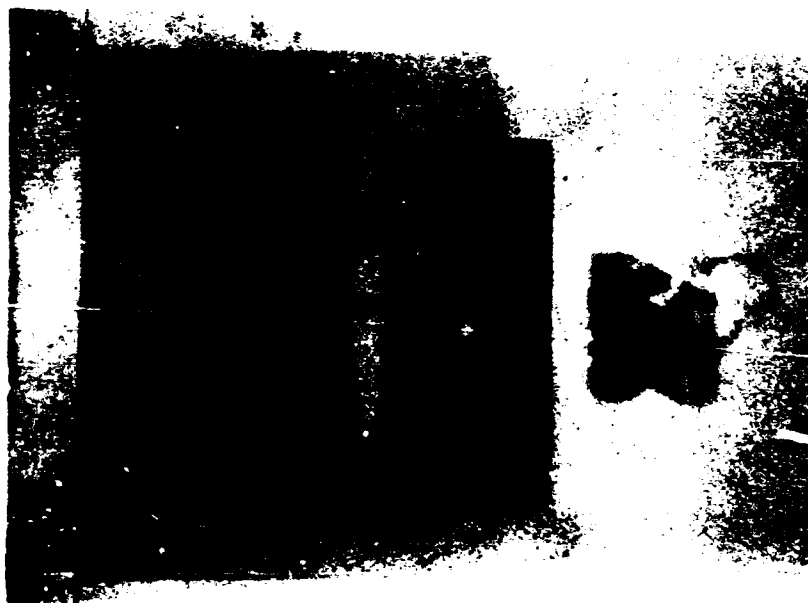


FIGURE 15 - CREVICE COUPON ASSEMBLY, NALCO
439 (1 MONTH EXPOSURE)



FIGURE 16 - CREVICE COUPON ASSEMBLY, SODIUM
NITRITE (1 MONTH EXPOSURE)

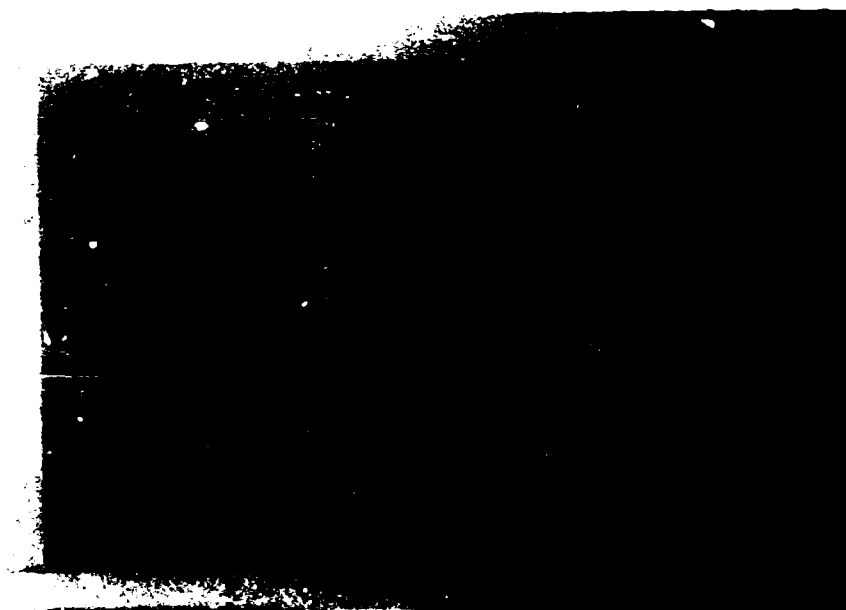


FIGURE 17 - CREVICE COUPON ASSEMBLY, SODIUM
NITRITE & EMULSIFIER STH
(1 MONTH EXPOSURE)

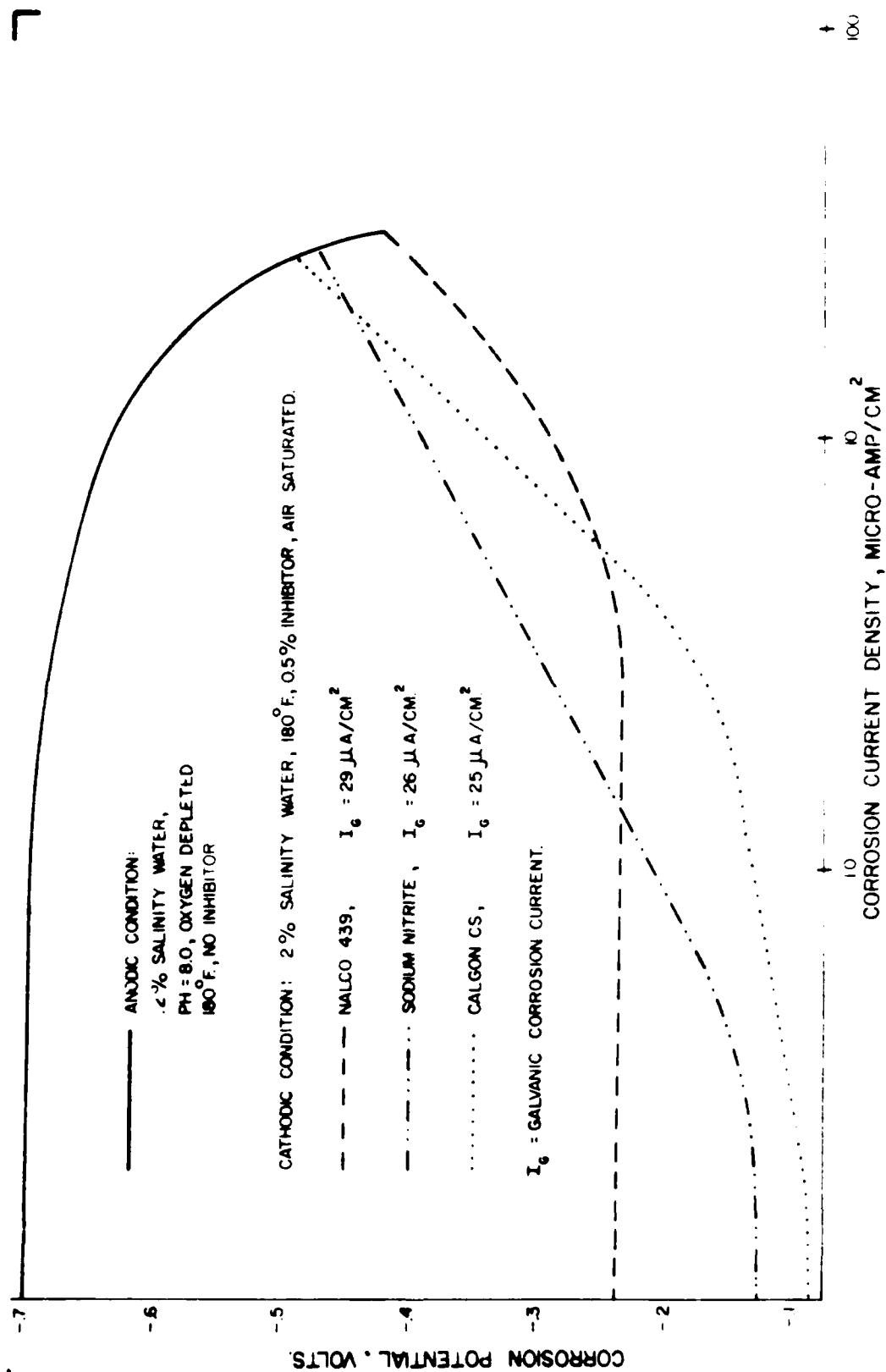


FIGURE -18 COMPOSITE PLOT OF POLARIZATION DATA FOR SAE 4340
 STEEL IN SIMULATED BRAKE WATER.

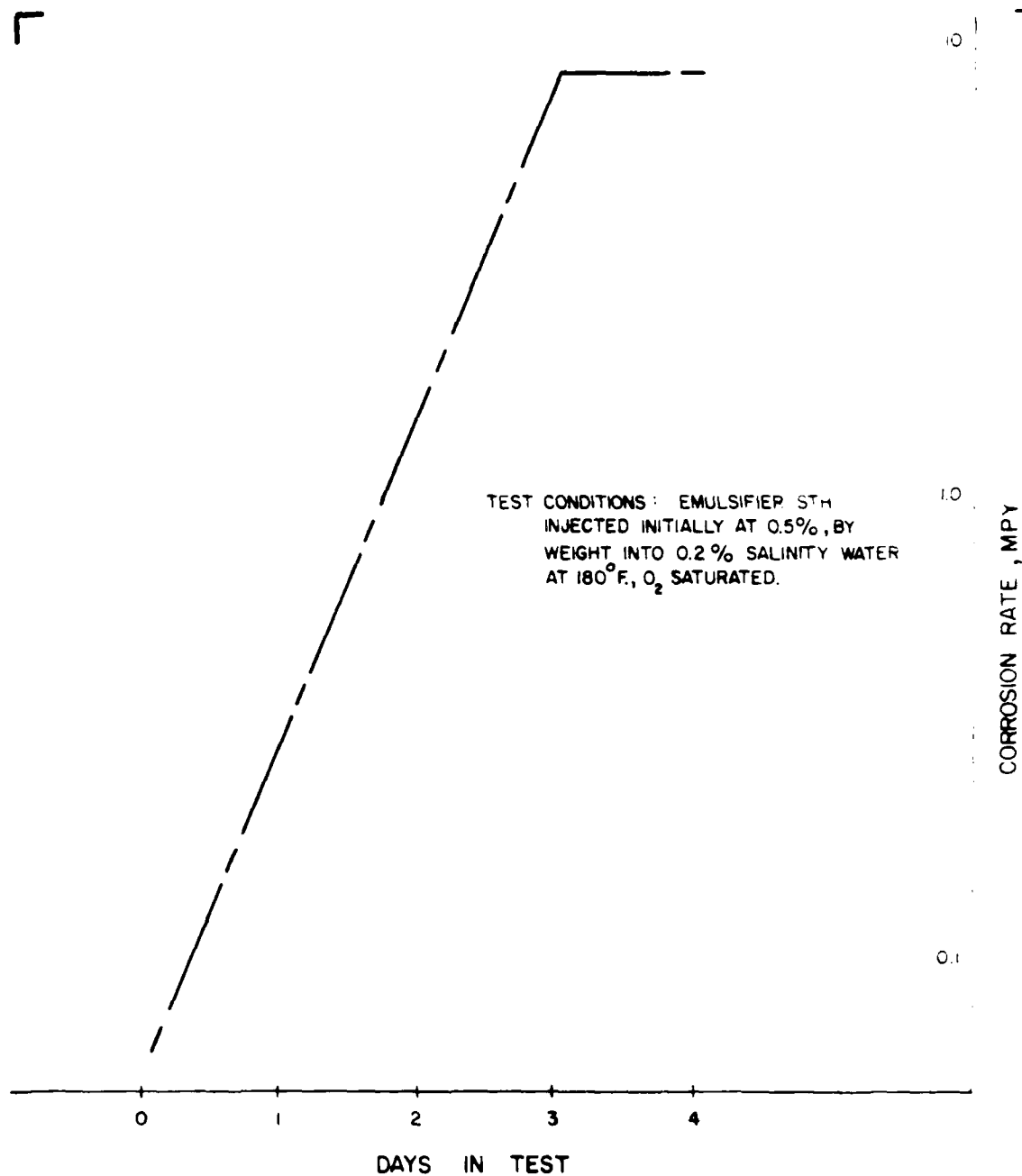


FIGURE 19 - CORROSION RATE VS. TIME, EMULSIFIER STH.

NOTE: ALLOY IDENTIFICATION IS GIVEN IN TABLE I.

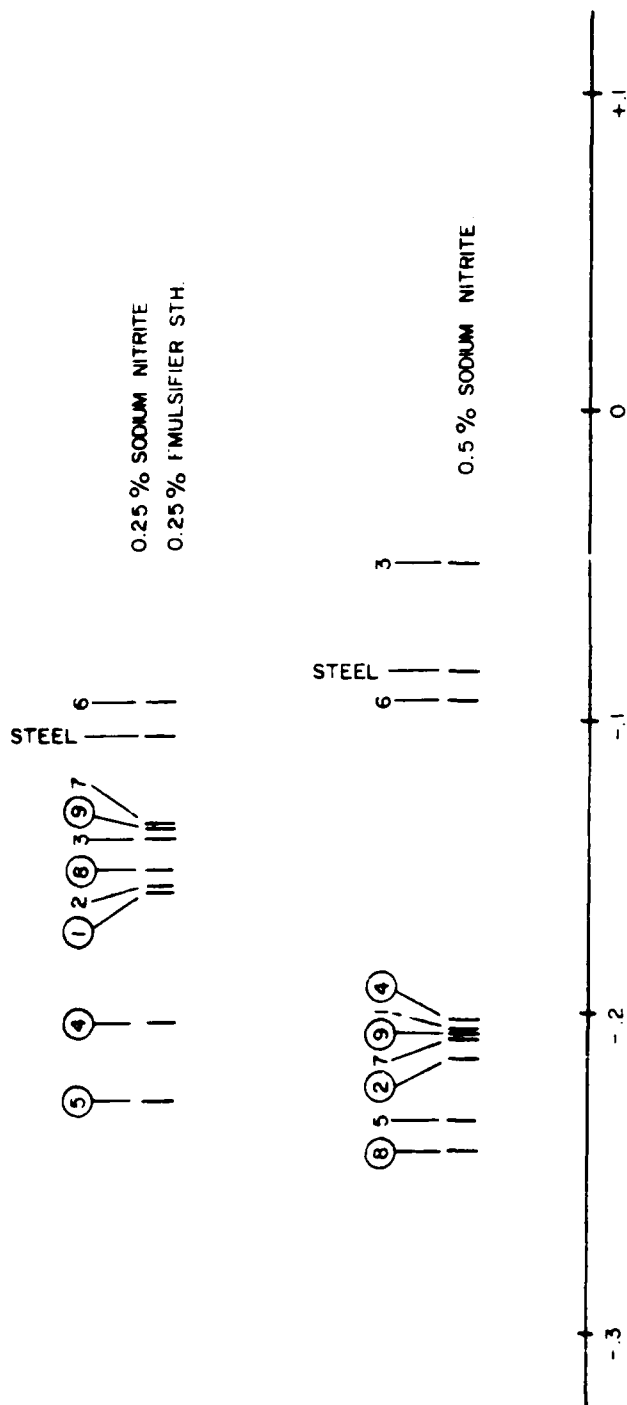


FIGURE 20 - CORROSION POTENTIAL, VOLTS, SHE., 180°F., 0.2 % SALINITY, AIR SATURATED.

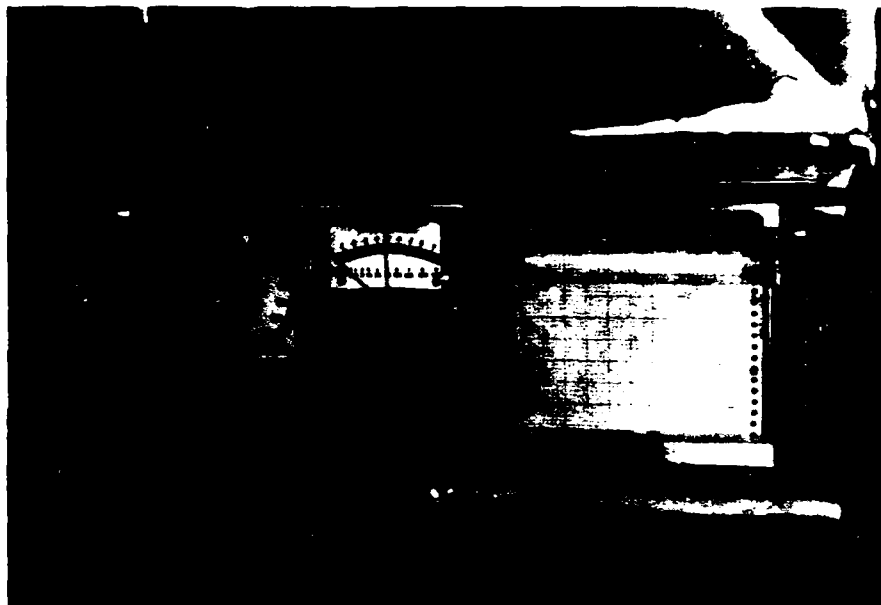


FIGURE 21 - CORROSION RATE MONITORING
INSTRUMENT

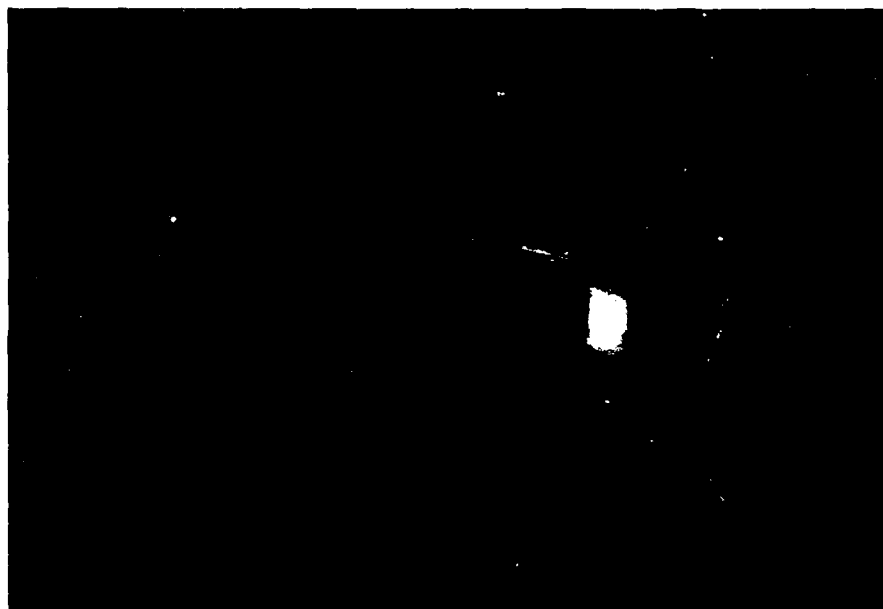
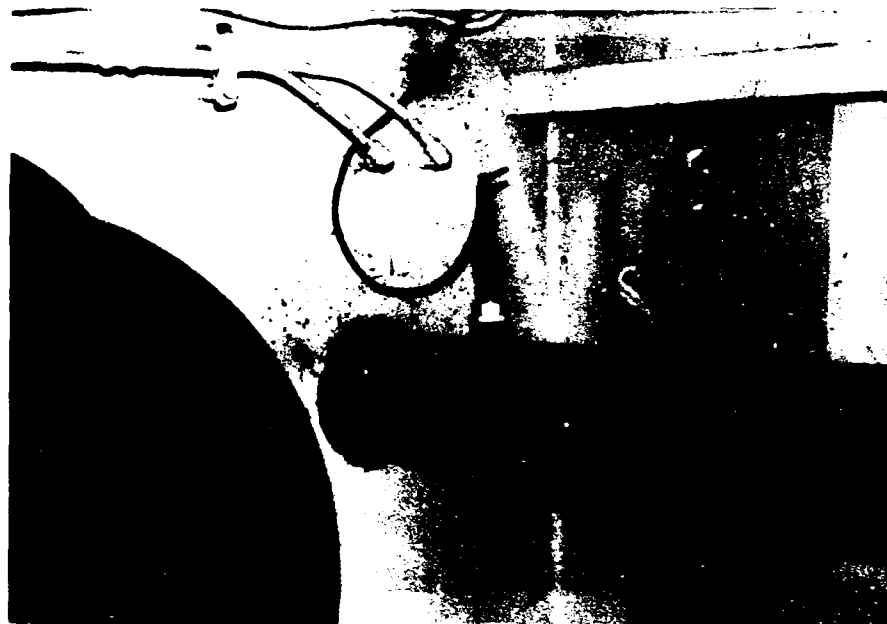


FIGURE 22 - SHIPBOARD INSTALLATION OF
INSTRUMENT



**FIGURE 23 - INSTALLATION OF SENSING PROBE
IN SUPPLY PIPE TO WATER BRAKE
NO. 3**



**FIGURE 24 - INSTALLATION OF SENSING PROBE
IN WATER BRAKE TANK NO. 3**

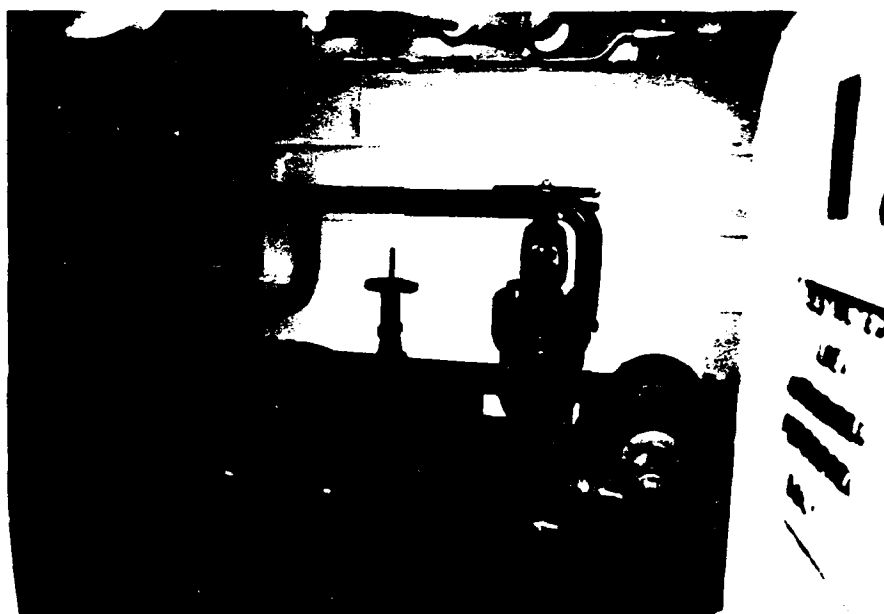


FIGURE 25 - WATER BRAKE COMPARTMENT



Figure 26 - Jet Ring From No. 3 Water Brake
on the CVA-64 After 12 Months
Operation with NaNO_2 Inhibitor



Figure 27 - Jet Ring From No. 4 Water Brake
on the CVA-64 After 12 Months
Operation Without Inhibitor

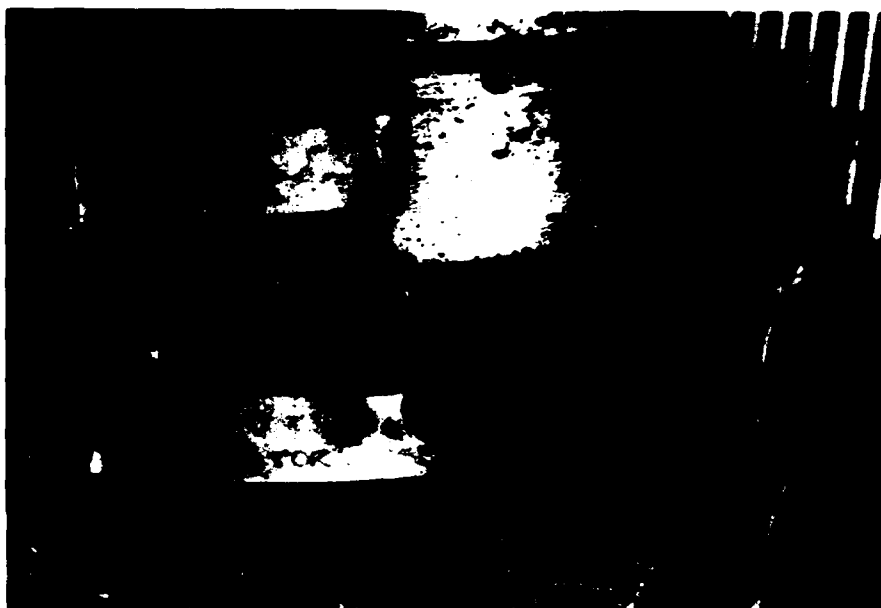


Figure 28 - Annulus Rings From Water Brakes
Nos. 3 & 4 on the CVA-64 After
12 Months Operation



Figure 29 - Striker Rings From Water Brakes
Nos. 3 & 4 on the CVA-64 After
12 Months Operation



Figure 30 - Striker Ring From Water Brake
No. 1 on CVA-64

APPENDIX A - The Use of Electrochemical Polarization Techniques to Measure Corrosion Rates

Advances in electrochemistry in recent years have evolved test techniques that overcome some of the limitations of simple weight loss measurements. Several techniques utilizing electrochemical measurements are now available to determine the corrosion rate of a metal exposed to a corrosive electrolyte.

When a metal is in a state of reversible equilibrium with a solution of its ions, simultaneous oxidation and reduction reactions are taking place with no net change in the weight of the metal electrode or the concentration of ions. The rate of oxidation and reduction taking place can be expressed in terms of Faraday's Law:

$$(1) \quad r_{\text{ox}} = r_{\text{red}} = i_0/nF$$

where i_0 is called the exchange current. Since oxidation current and reduction current have opposite polarities, at equilibrium there is no net current.

When the equilibrium of an electrode reaction is disturbed, there is a change in the potential of the electrode when measured against a stable reference. The difference between the equilibrium potential and the potential under the new conditions is called polarization and is usually designated by the Greek letter Eta, η . Mathematically:

$$(2) \quad \eta = E_{\text{eq}} - E$$

where E_{eq} is the potential at equilibrium and E is the potential under the new conditions. Disturbance of the equilibrium condition alters the exchange current balance and results in a net current flow, either oxidation or reduction, which is representative of the net rate of reaction. Polarization, therefore, results from any situation involving a net current flow to or from an electrode surface.

A metal undergoing corrosion involves two reactions, one at the cathode and one at the anode. Because of the current flow between local cathodes and anodes, a corroding metal polarizes toward a common potential, E_{cor} . The behavior of the corroding metal is studied by application of an external current. A measured and externally controlled source of direct current is connected between the corroding metal and a counter electrode. The change in potential (polarization) of the corroding metal is then determined as a function of the externally applied current, either anodic or cathodic.

The polarization resistance technique for determining corrosion rates involves polarizing a test specimen ± 20 millivolts from the corrosion potentials and measuring the currents associated with this partial polarization curve. Early researchers¹ thought that a linear relation existed between current and potential. They hypothesized that the slope of this "linear" polarization curve was inversely proportional to the corrosion rate according to the following expression:

$$(3) \quad \frac{\Delta E}{\Delta I} = \frac{1}{2.3} \times \frac{\beta_a \times \beta_c}{\beta_a + \beta_c} \times \frac{1}{I_c}$$

where I_c = corrosion current density
 β_a = Anodic Tafel Slope
 β_c = Cathodic Tafel Slope
 ΔI = Impressed Current Density
 ΔE = Polarization caused by impressed current
when $\Delta E < 20$ millivolts

The corrosion rate is a linear function of I_c according to Faraday's Law:

$$\text{corrosion rate} = \frac{K I_c}{\rho}$$

where k = electrochemical equivalent for specific metal
 ρ = density of specific metal

Recent work by Mansfield², however, demonstrates that there is no theoretical justification for polarization curves to be linear at or within ± 20 millivolts of the corrosion potential. He shows, in fact, that non-linearity is severe in many cases. This does not void, however, this polarization technique for determining corrosion rates. Mansfield shows that with some modification of data analysis, polarization curves within ± 20 millivolts of the corrosion potential can still be used as a basis for accurately calculating corrosion rates. The modifications include determination of $\frac{\Delta E}{\Delta I}$ @ $I = 0$ and application of curve fitting

techniques to more precisely determine β_a and β_c . The formula hypothesized by Stern is then shown to be valid.

¹M. Stern and A. L. Geary, "Electrochemical Polarization - Part 1", Jnl. Electrochemical Soc., 104, (1957).

²F. Mansfield, "Electrochemical Background of the Polarization Resistance Technique", a paper presented at the NACE Corrosion Conference, 1973.

APPENDIX B - Statistical Analysis of Stress Intensity Vs. Time-to-Failure Data

1. MPR-12 Alloy

For air fracture,

mean stress intensity = 121 ksi [in]^{.5}
 mean standard deviation = 15.2 ksi [in]^{.5}
 standard error of mean = 5.75 ksi [in]^{.5}

For fracture in .2% salinity water @ 180°F,

mean stress intensity = 111 ksi [in]^{.5}
 mean standard deviation = 8.4 ksi [in]^{.5}
 standard error of mean = 1.33 ksi [in]^{.5}

Estimating the significance of the difference in means,

standard error of difference = $[(5.75)^2 + (1.33)^2]^{.5}$

= 5.89

difference between means = 121 - 111

= 10

standardized deviate, t = 10 ÷ 5.89

= 1.69

No. of datum points for air fracture = 7

No. of datum points for fracture in .2%
 salinity water @ 180°F = 40

No. of degrees of freedom, $\phi = (7-1) + (40-1)$
 = 45

From Duckworth¹, for a t distribution, confidence
 level = 98%

2. SAE 4340 Alloy

For air fracture,

mean stress intensity = 90 ksi [in]^{.5}
 mean standard deviation = 10 ksi [in]^{.5}
 standard error of mean = 5 ksi [in]^{.5}

For fracture in .2% salinity water @ 180°F,

mean stress intensity = 75 ksi [in]^{.5}
 mean standard deviation = 7 ksi [in]^{.5}
 standard error of mean = 1.65 ksi [in]^{.5}

Estimating the significance of the difference in means,

$$\text{Standard error of difference} = [(5)^2 + (1.65)^2]^{.5}$$

$$= 5.25$$

$$\text{difference between means} = 90 - 75$$

$$= 15$$

$$\text{standardized deviate, } t = 15 \div 5.25$$

$$= 2.85$$

$$\text{No. of datum points for air fracture} = 4$$

$$\text{No. of datum points for fracture in } .2\%$$

$$\text{salinity water @ } 180^{\circ}\text{F} = 18$$

$$\text{No. of degrees of freedom, } \phi = (4-1) + (18-1)$$

$$= 20$$

From Duckworth¹, for a t distribution, confidence level = 99%

¹Duckworth, W. E., Statistical Techniques in Technological Research, Methuen & Co., London, 1968