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" C O P P E R L O K " C O A T I N G S Y S T E M

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FOREWARD

The subject program was funded through the Maritime Administration's National Shipbuilding Research Program. The program was administered by John Peart of Avondale Shipyards. The lead engineer on the program was G. A. Gehring, Jr. of the Ocean City Research Corp. All of the testing referenced in this report was conducted at the Ocean City Research Corp. laboratory in Ocean City, New Jersey.

The program had two principal objectives. The first was to determine the rate at which a proprietary coating (Copperlok) would corrode in seawater flowing a 30 feet per second (=18 knots); the second was to determine the effect of the Copperlok coating on corrosion of the steel substrate exposed at faults in the Copperlok coating, both with and without the Copperlok coating short circuited to the steel substrate.

EXECUTIVE SUMMARY

Fuel costs are now a major economic factor in the operation of all types of cargo ships. Fuel costs are recognized to account for no less than 50% of the total costs for operating a ship. Marine fouling of a ship's hull can significantly increase fuel consumption. Anti-fouling paints control fouling but, in general, their effectiveness decreases with time and re-painting becomes necessary, introducing another cost factor. These factors produce an incentive for the improvement of present anti-fouling paints and for the development of new and innovative coating systems.

Copperlok is one such innovative coating. The working part of the Copperlok system comprises a metallic, copper alloy coating applied by proprietary methods. The developers of the system recognized that the copper alloy would cause severe corrosion of steel hull if applied directly to it. Therefore, an insulating "tie coat" was developed that is applied to the hull prior to the application of the copper alloy topcoat.

The testing described in this report was conducted in the Ocean City Research Corporation seawater flow channel. Tests were conducted at a seawater velocity of 30 fps over a 63-day period using test panels supplied by Copperlok. The test results showed the corrosion/erosion rate of the coating to be about two mils per year at the completion of the 63-day period. The Copperlok had no significant effect on the rate at which the underlying steel corroded at intentional coating faults when there was no metallic electrical connection between the Copperlok and the steel. When there was an electrical connection between the copper coating and steel, the steel corroded at a very rapid rate. The following report describes the tests that were conducted and presents an analysis of the results.

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TECHNICAL APPROACH

General

Table 1 presents the general test plan that was followed. The original plan called for testing of two copper alloy coatings, CDA 706 and CDA 722. The coating applicator (Copperlok) was unable to obtain the CDA 722 alloy, so only a single alloy, CDA 706 was included in the tests.

TABLE 1 .

TEST SCHEME

o	Test Apparatus	OCRC Flow Channel
o	Test Velocity	30 fps (18 knots)
o	Test Duration	63 Days
o	Test Environment	Natural Seawater
o	Test Panels	5 Test Panels As Follows (1) Steel/Insulating. Tie-coat/CDA 706 Cu-Ni Both Sides. (2) & (3) Steel/Insulating Tie-Coat/CDA 706 Cu-Ni, One Side As-Applied, The Other Side With A 1/2" Diameter Holiday Centered On The Face Of The Panel. (4) & (5) Steel/Insulating Tie-Coat/CDA 706 Cu-Ni, One Side As-Applied, The Other Side With Nine 1/16" Diameter Holidays On 2" Horizontal Centers, 1" Vertical Centers.

Flow Channel

The OCRC flow channel is designed for corrosion/erosion studies, cavitation studies, and coating evaluations in natural seawater. The channel is capable of producing seawater velocities approaching 50 knots under realistic hydrodynamic conditions. The channel can accommodate a range of test specimen sizes from relatively small specimens to large test planks (1' x 10'). A double-suction centrifugal pump powered by a 100 horsepower motor circulates natural seawater through the channel at a flow rate exceeding 5,000 gallons per minute. The test portion of the channel has a rectangular cross-section. The channel width can be varied as required, thus producing the seawater velocity desired within the attainable range. Test specimens can be

fixtured in a slot along the centerline of the channel or integrally fitted in recesses machined in the sidewalls.

The channel is fabricated from two 8-inch steel channels bolted to 1/2-inch steel plate. Internally, the channel is lined with 1/2-inch acrylic plate and its removable top lid is 1-inch thick acrylic. This arrangement insures that the seawater does not contact the steel channel members. The channel design permits acquisition of electrochemical data by providing access for electrical connections to all test panels. The data so gathered provides an accurate measure of the rate at which the panels corrode during the course of testing.

The flow channel section that provides a 39 fps velocity was selected for the test described in this report. This velocity was selected since it is in the realistic range of typical ship speeds.

Test Panel Configuration

The internal vertical height of the channel section selected for the test is 7 inches with 1/2-inch wide grooves, 1/2-inch deep, top and bottom, on the horizontal center line. The groove is 58 inches long. The test panels were fabricated from steel plates (7-7/8" x 9-7/8" x 3/8" thick) with a total coating on all surfaces of approximately 1/16-inch wall thickness. The panel faces exposed to the flowing seawater were 7 inches x 10 inches. The panels therefore occupied 50 inches of the test section groove. A 1/2-inch thick nose piece was inserted ahead of the test panels to prevent seawater impingement directly upon the leading edge of the first test panel. The top edge of each panel was drilled and tapped at two locations. An 8-32 machine screw was used at each of these locations for the attachment of copper wire test leads. Two other test leads were soldered to the copper alloy coating of each test panel. The connections were epoxy coated to prevent contact between the conductor and seawater. The insulated copper wires were brought to the exterior of the flow channel through O-ring lid gaskets. As noted in Table 1, intentional holidays were drilled through both the copper alloy coating and the tie coat on certain panels, exposing the underlying steel panel.

Corrosion Rate Measurements

Two types of corrosion rate measurements were made during the course of the tests. Polarization resistance measurements, as described in Appendix I, were used to determine, individually, the rate at which copper alloy coating corroded and the rate at which the steel substrate corroded at the intentional holidays (with no electrical short circuit between the copper alloy coating and steel substrate).

The second type of measurement concerned the determination of the rate at which the steel substrate corroded at coating holidays with the copper alloy coating short circuited to the

copper alloy coating. Two methods were used. One method involved the measurement of the cathodic polarization characteristics of the copper alloy coating and the anodic polarization characteristics of the steel substrate. The maximum corrosion current that would flow under short circuit condition is the value determined by the intersection of the two polarization curves. The second method involved direct measurement of the galvanic corrosion current by connecting leads from the copper alloy coating and the steel panel through a zero resistance ammeter with a recorder output. The corrosion current values were recorded over a sufficient period so that reasonable stability was obtained.

Physical Measurement of Coating Thickness

There was no practical non-destructive way to measure, physically, the original thickness of the copper alloy coating. After completion of the tests, a Tooke gage was used to obtain a representative number of coating thickness measurements on each panel.

RESULTS

General

Figures 1 through 5 show the appearance of each of the test panels after the completion of 63 days' exposure in the seawater flow channel. Figure 1 is a photo of the panel with no holidays. Figures 2 and 3 show the panels with 1/16-inch diameter holidays. As apparent in Figure 3, the coating was removed in the vicinity of one of the holidays to determine if there was underfilm disbandment and/or accelerated corrosion of the substrate where it was exposed to the seawater. Neither significant disbandment nor corrosion was observed.

Figures 4 and 5 show the panels with 1/2-inch diameter holidays. The panel in Figure 5 was used for evaluating corrosion caused by short circuiting of the copper alloy coating with the steel substrate. The corrosion products heavily stained the copper alloy coating. The vertical staining occurred during the periods when the seawater was quiescent (i.e. when the main circulating pump was shut down to backwash upstream filters). This was about one hour of each day. The depth of corrosion measured on the substrate of the panel shown in Figure 4 is about 3 to 5 mils. This represents "an annual corrosion rate of between 18 and 30 mils. This range is not inconsistent with what would be expected for steel in seawater flowing at 30 feet per second. The sample shown in Figure 5, which was short circuited about 10 days, has substrate corrosion approaching 110 mils.

Prior to exposure, the copper alloy coating of all panels exhibited a rather rough surface. The roughness seemed unchanged when the panels were inspected after completion of the test run.

Corrosion Rate - Copper Alloy Coating

Figure 6 shows corrosion rates determined at different times during the test run. These rates are calculated from polarization resistance measurements as described in Appendix I. All plotted values are the average of two successive polarization resistance measurements. The initial value, ten days into the test run, is 16 mils/year. The final value, after 63 days' exposure, is 1.69 mils/year.

Coating Thickness Measurements

Coating thickness measurements after the conclusion of the test run did not yield quantitative results. The surface roughness of the coating was significant compared to the mean coating thickness. In general, the thickness ranged from 2 to 5 mils. There were many places where the coating residue did not have a metallic-appearing surface after being cut by the Tooke gage. The coating at these locations appeared to be comprised of only copper corrosion products.

Corrosion Rate At Coating Holiday, Copperlok Shorted To Steel

The majority of the data investigating this aspect were acquired on one of the panels with a 1/2-inch holiday. The initial evaluation of the probable severity of such corrosion was made by measuring the potential difference between the copper alloy coating and the steel substrate. This value was approximately 0.4 volt. The internal resistance between the copper alloy coating and the steel substrate was then measured. This value was found to be 71 ohms. The initial value of current that would flow if the two were short-circuited would be the open-circuit potential, 0.4 volts, divided by the internal resistance, 71 ohms. This gives a calculated value of 5.6 milliamps. The surface area of the 1/2-inch diameter holiday is 0.00136 square feet. This calculated corrosion current is an exceptionally high value, indicating an initial corrosion rate of 2.22 inches per year. Under most circumstances this value would be expected to decrease with time because of the polarization characteristics of the anodic and/or cathodic surfaces.

In order to evaluate this possibility, we conducted further tests to determine the anodic polarization characteristics of the steel substrate at the holiday and the cathodic polarization characteristics of the copper alloy coating. Figure 7 shows the plots of the anodic polarization curve for the steel at the 1/2-inch holiday and the cathodic polarization curve for the copper alloy coating of one of the test panels. The cathodic curve for the copper alloy is typical. The anodic curve for the steel shows an unusual behavior, becoming unstable at values about 1.5 milliamps (1.1 amps/sqft). Supplementary measurements showed that the resistance of the exposed metal to its environment also became unstable above this range, indicating surface film breakdown.

In order to clarify the situation, the actual short-circuit current flow for this panel was measured, as a function of elapsed time, by using a potentiostat to hold the voltage difference between the copper alloy and the steel substrate to zero while recording the value of current required to accomplish this. The current value stabilized very rapidly at approximately 3 milliamps. This is a current density of about 2.2 amps/sqft which corrodes steel at a rate of about one inch/year.

CONCLUSIONS

1. The Copperlok coating, as applied and tested in this program, will not accelerate corrosion of a steel substrate at holidays. An exception might be turbulence-induced corrosion caused by a sharp edge or step at the leading edge of the holiday.
2. The Copperlok coating will cause extremely rapid corrosion of the steel substrate at coating holidays if the copper alloy coating is short-circuited to the steel substrate.
3. The long-term corrosion rate of the copper alloy coating will approximate 1.5-2.0 mils per year when the ship speed is about 18 knots. Higher corrosion rates would be expected at higher speeds, lower corrosion rates at lower speeds.
4. There seemed to be no significant change of surface roughness of the copper alloy coating between the beginning and end of the 63-day test.

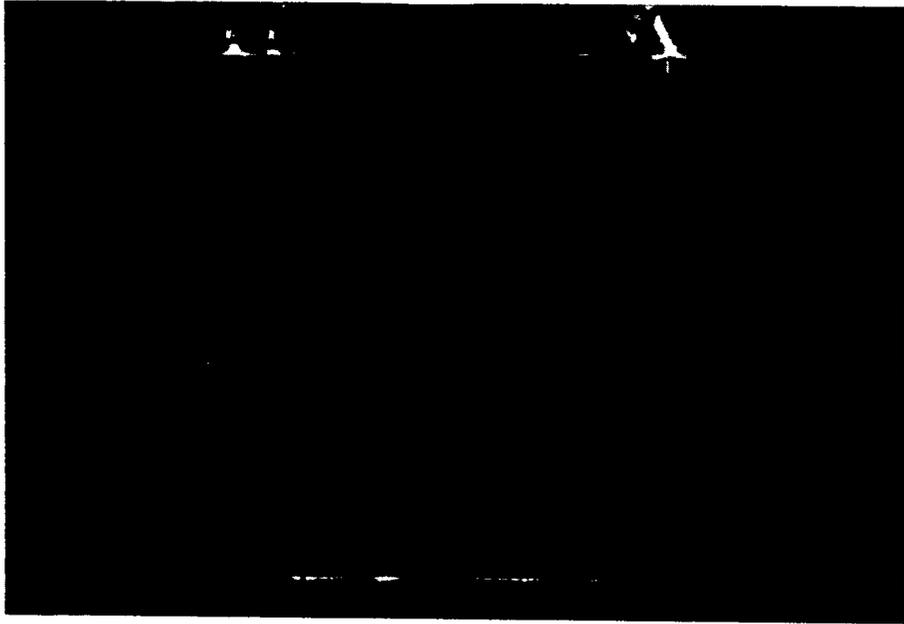


Figure 1.

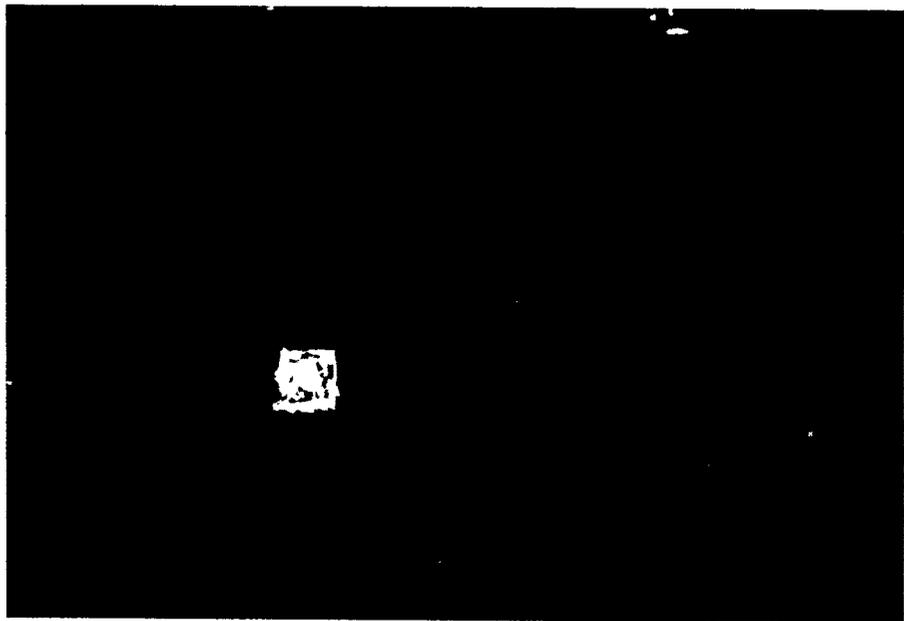


Figure 2.

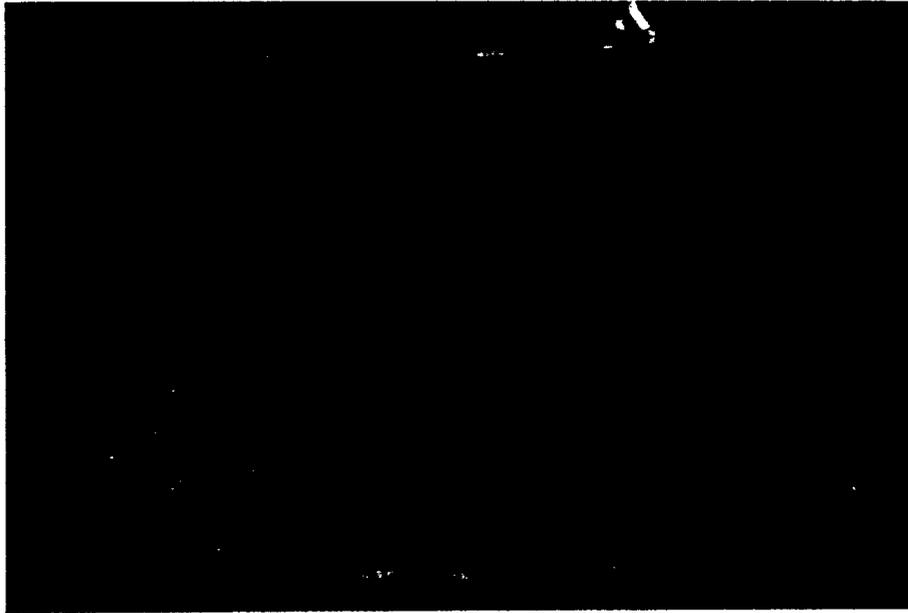


Figure 3.



Figure 4.



Figure 5.

Figure 6.

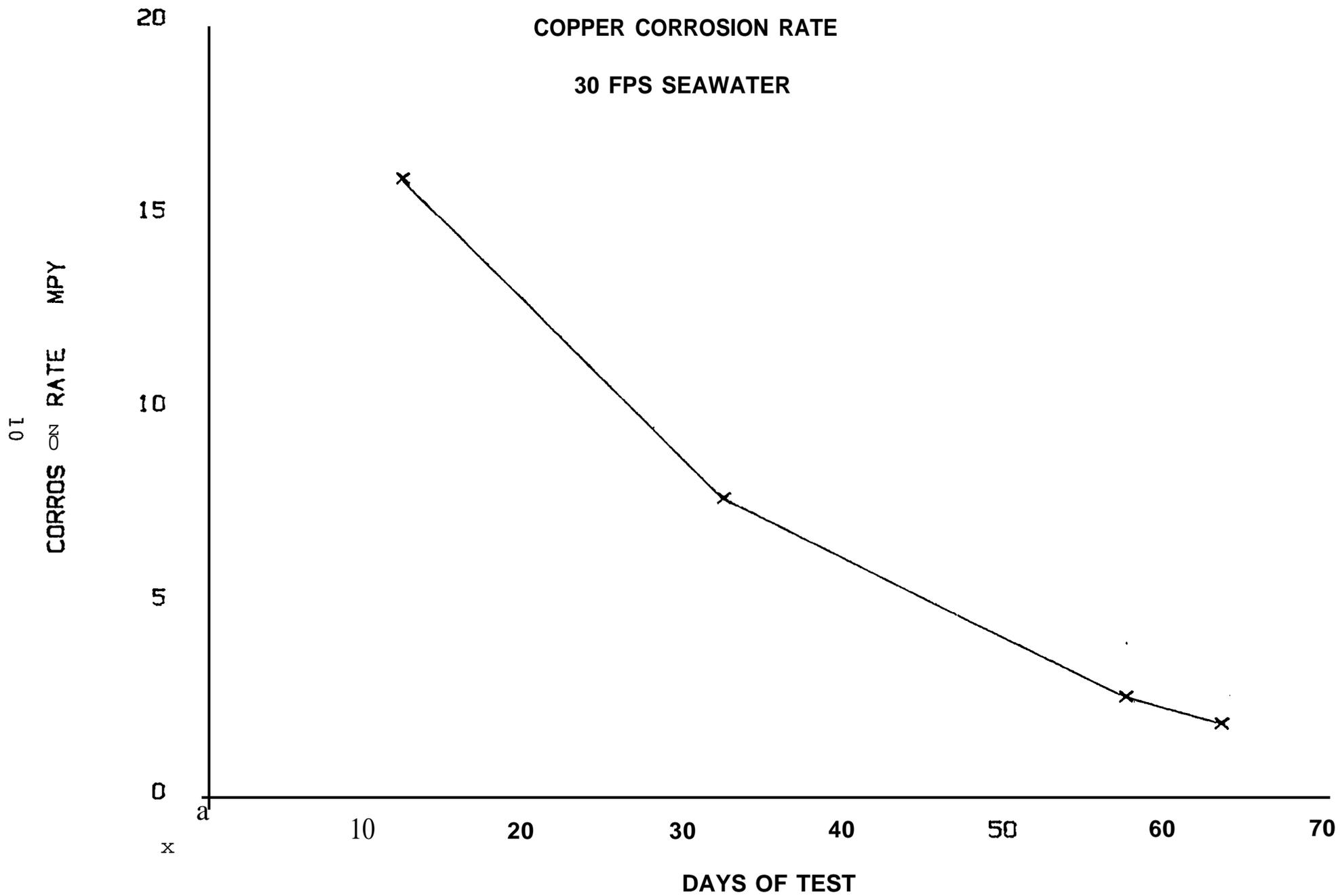
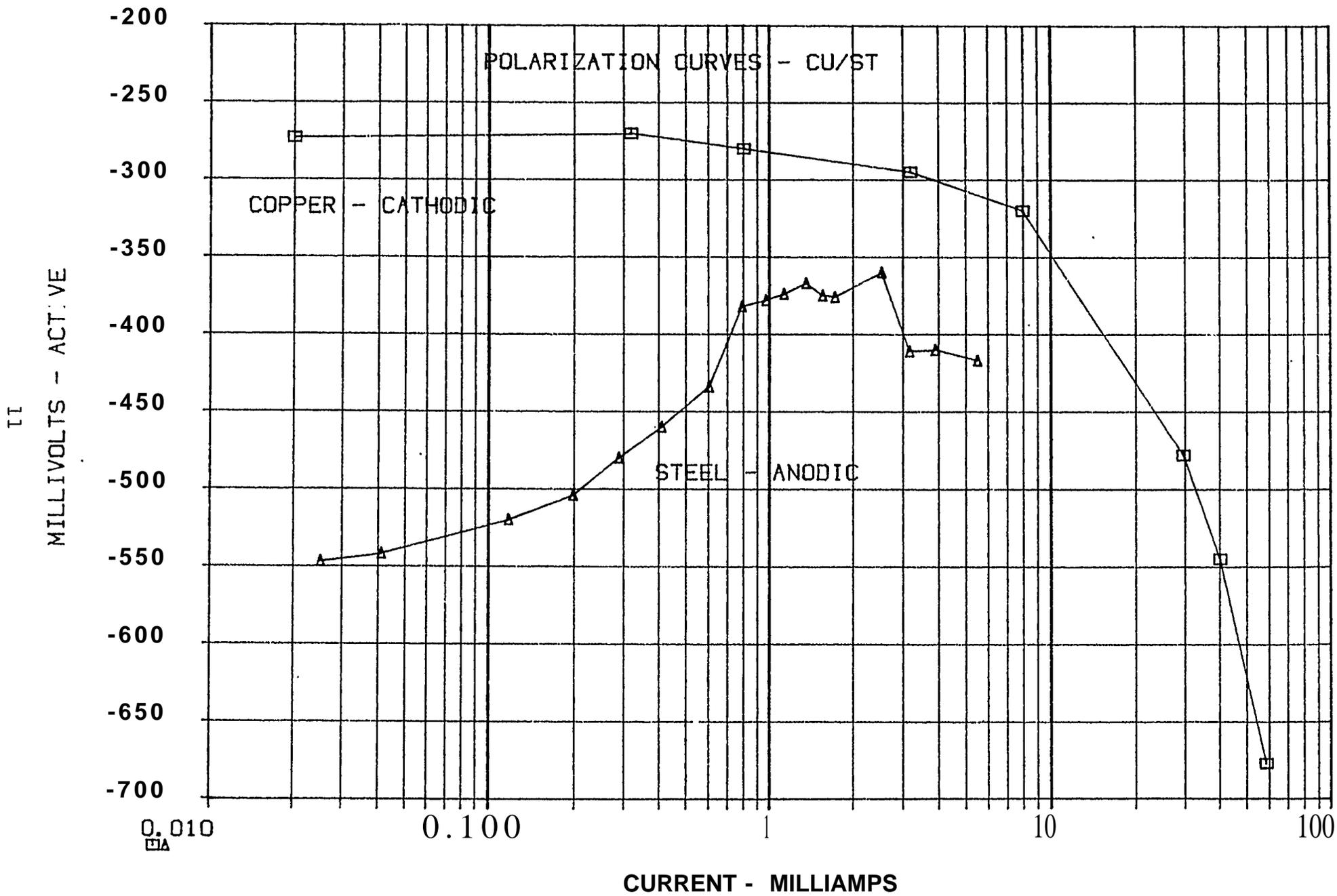


Figure 7.



Log

Appendix I

Appendix I

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:

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

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 "linear" polarization technique for determining corrosion rates involves polarizing a test specimen ± 20 millivolts from the corrosion potential and measuring the currents associated with this partial polarization curve. Early researchers (1) 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:

$$\text{corrosion rate} = kI_c$$

where, k = electrochemical equivalent for specific metal

ρ = density of specific

Work by Mansfeld (2), however, demonstrated that there was no theoretical justification for polarization curves to be linear at or within ± 20 millivolts of the corrosion potential. He showed, in fact, that non-linearity is severe in many cases. This does not void, however, this polarization technique for determining corrosion rates. Mansfeld showed 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 P_a and P_c . The formula hypothesized by Stern is then shown to be valid.

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1. Stern and A.L. Geary, "Electrochemical polarization - part 1", Jnl. Electrochem. Soc., 104, (1957).
 2. Mansfeld, "Electrochemical Background of the Polarization Resistance Technique", Corrosion, 29, (1973).