

Inhibition of Heavy Metal Ion Corrosion on Aluminum in Fresh Water Cooling Systems
Using Propylene Glycol Anti-Freeze

by Harvey P. Hack
Northrop Grumman Corp.
Electronic Sensors and Systems Division
P. O. Box 1488, Mail Stop 9105
Annapolis, MD 21404

Richard Corbett, and Brad Krantz
Corrosion Testing Labs
60 Blue Hen Drive
Newark, DE 19713

ABSTRACT

Electronics cooling and environmental control systems are required in enclosed manned spaces such as the inside of spacecraft or submersibles. Because egress from such spaces may not be possible in a short time frame, coolant leaks must have minimum toxicity. For this reason, propylene glycol coolants are preferred over the traditional ethylene glycol coolants. Corrosion inhibitor formulations are well developed for ethylene glycol coolants, but there is concern that the inhibitor suite for propylene glycol systems may not be as mature. In particular, coolant systems with a mixture of aluminum and copper can develop heavy metal ion corrosion of the aluminum due to precipitation of copper ions from solution onto the aluminum. This type of accelerated corrosion of aluminum does not require electrical contact with copper, as is the case for galvanic corrosion, nor is significant coolant conductivity required for corrosion to occur. This paper presents a study of the ability of a commercial inhibited propylene glycol coolant to prevent heavy metal ion corrosion of aluminum when copper is also present in the coolant system. The inhibited propylene glycol's performance is compared to that of reagent propylene glycol without inhibitors, a mature ethylene glycol inhibited coolant, and to tap water. The inhibitor suite in the inhibited propylene glycol was found to be as effective in controlling heavy metal ion corrosion as that of the inhibited ethylene glycol coolant, while uninhibited reagent propylene glycol was ineffective in controlling heavy metal ion corrosion.

Keywords: propylene glycol, ethylene glycol, inhibitors, engine coolants, 6061 aluminum, 3003 aluminum, pitting, heavy metal ion corrosion

INTRODUCTION

Electronics cooling and environmental control systems are required in enclosed manned spaces such as the inside of spacecraft or submersibles. Because egress from such spaces may not be possible in a short time frame, coolant leaks must have minimum toxicity. The traditional water-based coolants for engine use contain ethylene glycol, which is toxic if ingested and may cause respiratory distress if the fumes are inhaled for extended periods. Some newer coolants contain propylene glycol, which is non-toxic. For this reason, propylene glycol coolants are preferred over the traditional ethylene glycol coolant systems for use in submersibles.

Publication Right

Government work published by NACE International with permission of the author(s). Requests for permission to publish this manuscript in any form, in part or in whole must be made in writing to NACE International, Publications Division, P.O. Box 218340, Houston, Texas 77218-8340. The material presented and the views expressed in this paper are solely those of the author(s) and are not necessarily endorsed by the Association. Printed in the U.S.A.

Coolant systems with a mixture of aluminum and copper can develop heavy metal ion corrosion of the aluminum due to precipitation of copper ions from solution onto the aluminum^{1,2}. This type of accelerated corrosion of aluminum does not require electrical contact with copper, as is the case for galvanic corrosion, nor is significant coolant ionic conductivity required for corrosion to occur. To minimize this type of corrosion in automotive engines, inhibitor formulations have been developed and optimized over the years for ethylene glycol coolants. Northrop Grumman Corporation had a concern that the inhibitor suite for the newer propylene glycol based coolants may not be as mature. For this reason, testing of one commercial inhibited propylene glycol based coolant system was undertaken to determine the corrosion inhibition effectiveness of its proprietary inhibitor suite. The inhibitor performance was compared to that of the mature inhibitor suite in an inhibited ethylene glycol based coolant, to reagent grade propylene glycol without inhibitors, and to tap water without inhibitors.

MATERIALS

Aluminum mass loss coupons, 1 X ¾ X 1/16-in (2.5 X 1.9 X 0.16-cm) were prepared from 6061-T6 aluminum sheet, and aluminum electrochemical test coupons, 3/8 X 5/8 X ¼-in (0.95 X 1.6 X 0.64-cm) were prepared from 3003 aluminum plate. Copper alloy coupons were used in some exposures as a source of copper ions to cause heavy metal ion corrosion of the aluminum. Copper mass loss specimens, 1 X ¾ X 1/16-in (2.5 X 1.9 X 0.16-cm) were prepared from alloy 110 copper sheet and copper electrochemical specimens, 3/8 X 5/8 X ¼-in (0.95 X 1.6 X 0.64-cm) were prepared from alloy 110 copper plate.

EQUIPMENT

Electrochemical data was collected using a Gamry PC3 potentiostat board installed into a generic 486 computer and a Gamry ECM 8 multiplexer to allow automated collection of data from several test cells without user intervention. The reference electrodes used were silver/silver chloride electrodes in a salt bridge containing saturated KCl. The counter electrodes used were carbon rods.

EXPERIMENTAL PROCEDURE

Aluminum alloy mass loss coupons were prepared to a 120 grit surface finish, cleaned with nitric acid, massed and measured prior to exposure. Aluminum alloy electrochemical coupons were prepared to a 320 grit finish, cleaned with nitric acid, massed and measured prior to exposure. Copper alloy mass loss coupons were prepared with the as-rolled surface unmodified, cleaned with hydrochloric acid, massed and measured prior to exposure. Copper alloy electrochemical coupons were prepared to a 320 grit finish, cleaned with hydrochloric acid, massed and measured prior to exposure. The aluminum and copper alloy electrochemical specimens were then attached to electrode holders similar to those described in ASTM Standard Method G5.

Aluminum alloy mass loss and electrochemical specimens were exposed in each test solution in a polypropylene beaker either by themselves, or in the same beaker with copper mass loss and electrochemical specimens which were not in electrical contact with the aluminum. In this way, the effect of the copper ions from the corroding copper could be evaluated. The test solutions used were: 1) Newark, Delaware tap water, 2) a 30% solution of reagent grade propylene glycol in de-ionized water, 3) a 30% solution of Prestone® antifreeze in de-ionized water, and 4) a 30% solution in de-ionized water of Sierra® antifreeze-coolant, manufactured by Safe Brands Corporation, 727 South 13th Street, Omaha, NB 68102. The test solutions were heated to 150°F (66°C) and stirred continuously with magnetic stirrer bars at approximately 20 revolutions/minute.

Open circuit potentials were monitored for the first two hours of exposure. Then the polarization resistance of each electrochemical specimen in each exposure condition was measured. Additional open circuit potential monitoring and polarization resistance measurements were conducted at days 8, 21, 31, 61, and 91. These measurements were typically carried out from -20-mV to +20-mV relative to the open circuit potential at a scan rate of 0.167-mV/s, although for a few measurements, a slightly wider potential range was used, and for some scans rates up to 0.5-mV/s were used. These variations in test procedure appeared to have little influence on the results. From these measurements, the instantaneous corrosion rate at the measurement time was calculated.

A copper analysis of each of the test solutions containing copper was carried out after one month and at the conclusion of the exposures. This analysis was performed with a Hach DR/2000 Spectrophotometer. Fresh solution was

added to each test cell to make up for the solution removed for analysis. An additional copper analysis was performed after two months on the tap water containing copper coupons due to the low rate of aluminum corrosion being experienced. The analysis indicated a lack of copper in solution, possibly due to passivation of the copper, so an additional copper coupon was added to every test cell that contained copper.

The exposures were carried out for a total of three months (91 days). At the conclusion of the exposures, the mass loss specimens were removed and polarization curves of both aluminum and the copper alloy were measured from -300-mV to +300-mV relative to the open circuit potential at a scan rate of 0.167-mV/s. The electrochemical specimens were next removed and all samples were photographed, visual observations noted of corrosion products or scales, cleaned per ASTM Standard Procedure G1, massed to calculate mass loss and pit depths and distributions measured on the aluminum alloy where appropriate per ASTM Standard Procedure G46.

RESULTS

Table 1 shows the visual observations made before cleaning. Differences in appearance between electrochemical and mass loss specimens were slight, and are not indicated in the table. Table 2 shows the visual observations and pit measurements made on the mass loss specimens after cleaning. Table 3 shows the visual observations and pit measurements made on the electrochemical specimens after cleaning. The maximum pit depths listed are in mils and the pitting densities are based on visual comparison with the pitting density chart in ASTM Practice G46. Table 4 gives the analyses of the copper ions in the various test solutions. Table 5 presents the mass losses for the electrochemical and mass loss specimens. Table 6 presents the results of the polarization resistance measurements on the aluminum alloy. The results have been converted to corrosion rates in units of mils/yr.

The open circuit potential of aluminum immersed in the inhibited coolants became more electropositive than those immersed in the uninhibited solutions, and stayed in this relative position until the end of the test, when potentials in tap water inexplicably drifted positive. Throughout most of the test, the order of the open circuit potentials from most positive to most negative was: inhibited propylene glycol>inhibited ethylene glycol>reagent propylene glycol>tap water.

Polarization curves for aluminum and copper alloy are presented in Figures 1-3. Figure 1 shows the curves for the aluminum alloy in test solutions without copper present. Figure 2 shows the curves for the aluminum alloy in test solutions with copper present, and Figure 3 shows the curves for the copper alloy.

DISCUSSION

The integrated instantaneous corrosion rates were a factor of 20-40 lower than the corrosion rates actually measured by mass loss. This could be due to the localized nature of the attack or to non-electrochemical metal removal by "grain dropping". The trends in behavior are similar, however. The polarization resistance instantaneous corrosion rates are plotted in Figure 4 for the materials in solutions without copper. Both inhibited coolants were effective in reducing the corrosion rate of the aluminum alloys to essentially zero, while corrosion rates in tap water and reagent propylene glycol were only minimal when copper ions were not present in solution. This observation is consistent with visual observations, pitting measurements, and mass loss data. The polarization resistance corrosion rates are plotted in Figure 5 for the materials in solutions with copper. Again, both inhibited coolants kept the corrosion rate of the aluminum alloys to essentially zero, and again, this is consistent with visual observations, pitting measurements, and mass loss data. The presence of copper metal in the reagent grade propylene glycol solution caused copper ions to build up to a significant level in solution as copper corrosion occurred, which in turn caused significant pitting corrosion on the aluminum alloy in these test cells. Corrosion of either aluminum alloy in this case would be considered unacceptable for most applications. A similar buildup in copper ion concentration did not occur in tap water, possibly due to the black tenacious deposit that formed on the copper coupons. For that reason, the corrosion of the aluminum alloys was not as intense in this environment as in the reagent grade propylene glycol. Still, the aluminum alloy experienced more corrosion than if the copper had not been present, and the amount of pitting was significant for most applications where coolant would have to be retained for some period of time by the aluminum. The performance of the inhibitors in these tests does not necessarily indicate how they would perform under heat transfer conditions, or after long periods of time.

CONCLUSIONS

- Cooling systems containing both copper and aluminum require some form of corrosion inhibitors to prevent heavy metal ion corrosion of the aluminum by the copper, even if the two metals are not in electrical contact and do not experience galvanic effects.
- An uninhibited 30% reagent grade propylene glycol solution in water at 150°F (66°C) was sufficiently corrosive to copper to cause high concentrations of copper ions to build up in the coolant, causing unacceptably high pitting corrosion of aluminum alloys 6061 and 3003.
- Newark, Delaware tap water at 150°F (66°C) caused a tenacious black deposit to form on copper, lowering its corrosion rate significantly compared to reagent propylene glycol. There was still sufficient copper to cause pitting corrosion of aluminum alloys 6061 and 3003 however.
- The mature inhibitor suite in the inhibited ethylene glycol antifreeze was sufficient to prevent pitting of aluminum alloys at 150°F (66°C), even when copper ions were present.
- The inhibitors in the inhibited propylene glycol antifreeze-coolant were as effective as those in the inhibited ethylene glycol in preventing pitting of aluminum alloys at 150°F (66°C), even when copper ions were present.
- The performance of the inhibitors in these tests does not necessarily indicate how they would perform under heat transfer conditions, or after long periods of time.

REFERENCES

1. Uhlig, H. H., The Corrosion Handbook, ©1948, John Wiley and Sons, Inc., New York, NY, p. 47.
2. "Corrosion of Aluminum and Aluminum Alloys," Hollingsworth, E. H., Hunsicker, H. Y., Metals Handbook - Ninth Edition - Volume 13 - Corrosion, ©1987, ASM International, Metals Park, OH, p. 589.

3. TABLE 1
VISUAL OBSERVATIONS BEFORE CLEANING

	Aluminum (no copper present)	Aluminum (copper present)	Copper
Tap Water	heavy white corrosion deposit and pitting	heavy white corrosion deposit and pitting	black tenacious deposit
30% Reagent Propylene Glycol	gray surface oxide, one possible deep pit	reddish-brown and white corrosion deposit, extensive pitting	white deposit over a reddish-brown layer
30% Inhibited Propylene Glycol	no deposits, no corrosion	small spots of white corrosion deposit, possible small pits and crevice corrosion	bright and shiny, no corrosion
30% Inhibited Ethylene Glycol	several small spots with white deposits	light green tinted surface, no corrosion	bright and shiny, no corrosion

TABLE 2
VISUAL OBSERVATIONS AND PIT MEASUREMENTS OF MASS LOSS SPECIMENS AFTER CLEANING

	Aluminum (no copper present)			Aluminum (copper present)			Copper
	Corrosion Type	depth	density	Corrosion Type	depth	density	Corrosion Type
Tap Water	uniform, pitting	2	4	uniform, pitting	<1	2	uniform
30% Reagent Propylene Glycol	pitting	4	1	uniform, pitting	15	3	uniform
30% Inhibited Propylene glycol	uniform	-	-	uniform	-	-	uniform
30% Inhibited Ethylene Glycol	uniform	-	-	pitting	<1	1	uniform

TABLE 3
VISUAL OBSERVATIONS AND PIT MEASUREMENTS OF ELECTROCHEMICAL SPECIMENS AFTER CLEANING

	Aluminum (no copper present)			Aluminum (copper present)			Copper
	Corrosion Type	depth	density	Corrosion Type	depth	density	Corrosion Type
Tap Water	uniform, pitting	10	2	uniform, pitting	17	2	uniform
30% Reagent Propylene Glycol	pitting	18	1	uniform, pitting	>50	3	uniform
30% Inhibited Propylene Glycol	pitting	<1	1	pitting	14	1	uniform
30% Inhibited Ethylene Glycol	pitting	<1	1	pitting	<1	1	uniform

TABLE 4
COPPER ION ANALYSIS RESULTS, mg/L

	1 Month	2 Months	3 Months
Tap Water	0.1	0.1	1.0
30% Reagent Propylene Glycol	110		250
30% Inhibited Propylene Glycol	0.2		5.4
30% Inhibited Ethylene Glycol	0.6		<0.1

TABLE 5
CORROSION RATES OBTAINED FROM MASS LOSS, mils/yr

	Aluminum (no copper present)		Aluminum (copper present)		Copper	
	Electrochem	Mass Loss	Electrochem	Mass Loss	Electrochem	Mass Loss
Tap Water	3.2	1.8	2.0	1.0	0.1	0.1
30% Reagent Propylene Glycol	0.3	0.1	88.0	46.0	3.3	5.0
30% Inhibited Propylene Glycol	0.0	0.0	0.0	0.0	0.1	0.1
30% Inhibited Ethylene Glycol	0.0	0.0	0.1	0.0	0.05	0.1

TABLE 6
CORROSION RATES OF ALUMINUM FROM POLARIZATION RESISTANCE MEASUREMENTS, mils/yr

Solution	< 1 Days Exposure		8 Days Exposure		21 Days Exposure		31 Days Exposure		61 Days Exposure		91 Days Exposure	
	No Cu	Cu	No Cu	Cu	No Cu	Cu	No Cu	Cu	No Cu	Cu	No Cu	Cu
Tap Water	.130	.668	.031	.016	.075	.177	.240	.033	.296	.002	.156	.007
30% Reagent Propylene Glycol	.064	.354	.003	.090	.019	.379	.019	.644	.140	6.23	.018	.712
30% Inhibited Propylene Glycol	.007	.003	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
30% Inhibited Ethylene Glycol	.011	.005	.000	.000	.000	.000	.000	.001	.000	.003	.000	.002

220/7

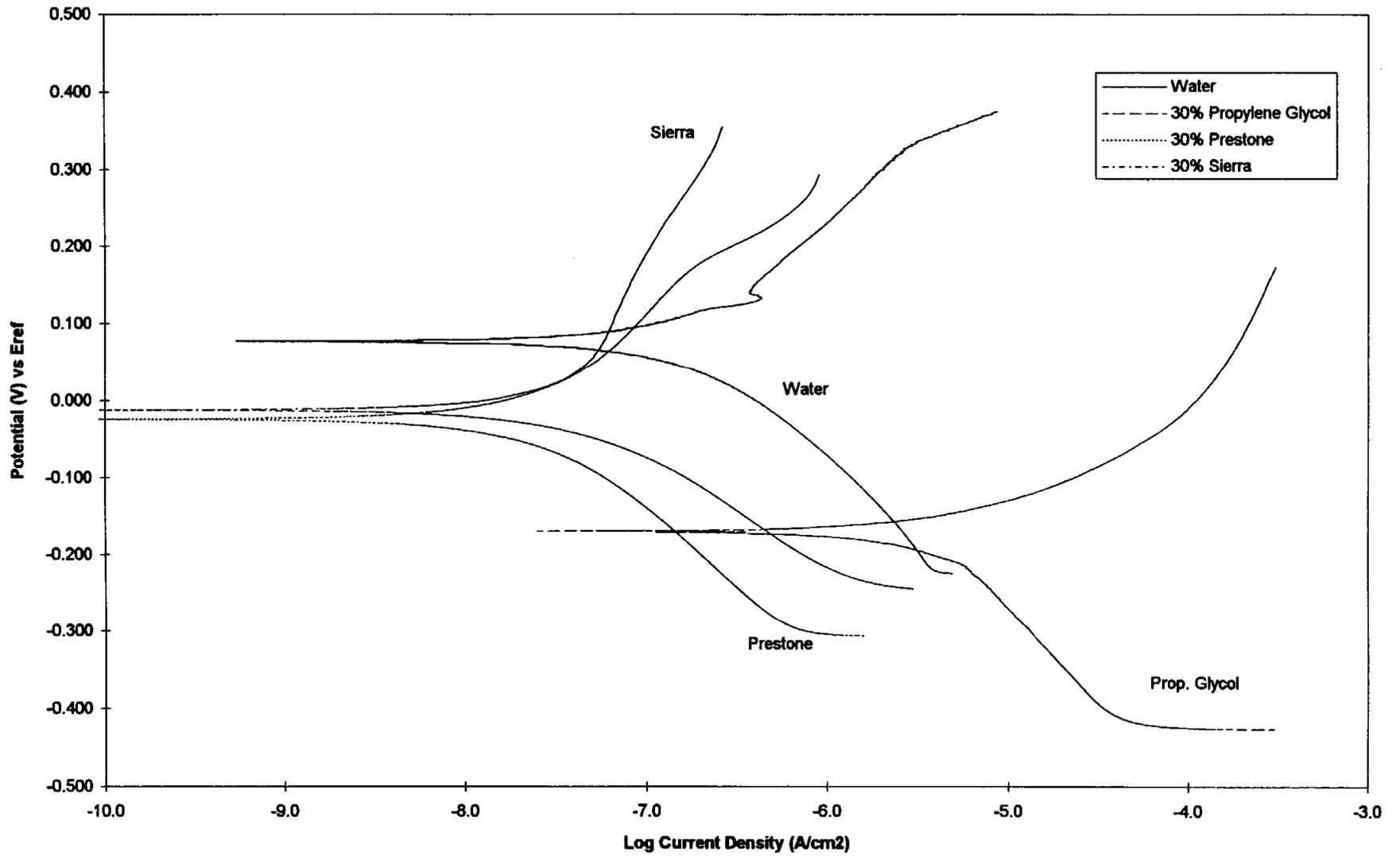


FIGURE 1 - Polarization of 3003 Aluminum in Coolant at 150°F Without Copper Present

220/8

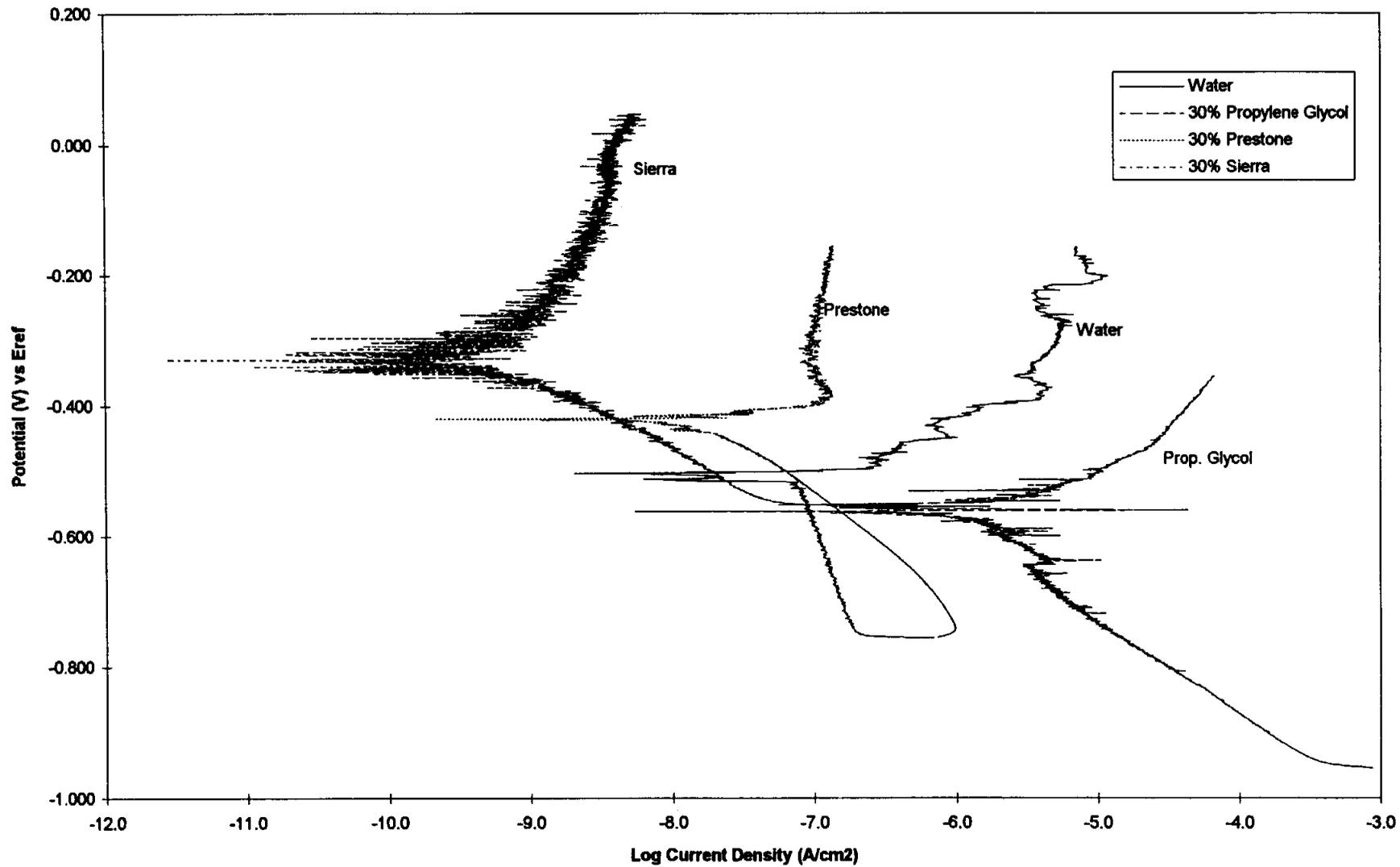


FIGURE 2 - Polarization of 3003 Aluminum in Coolant at 150°F With Copper Present

220/9

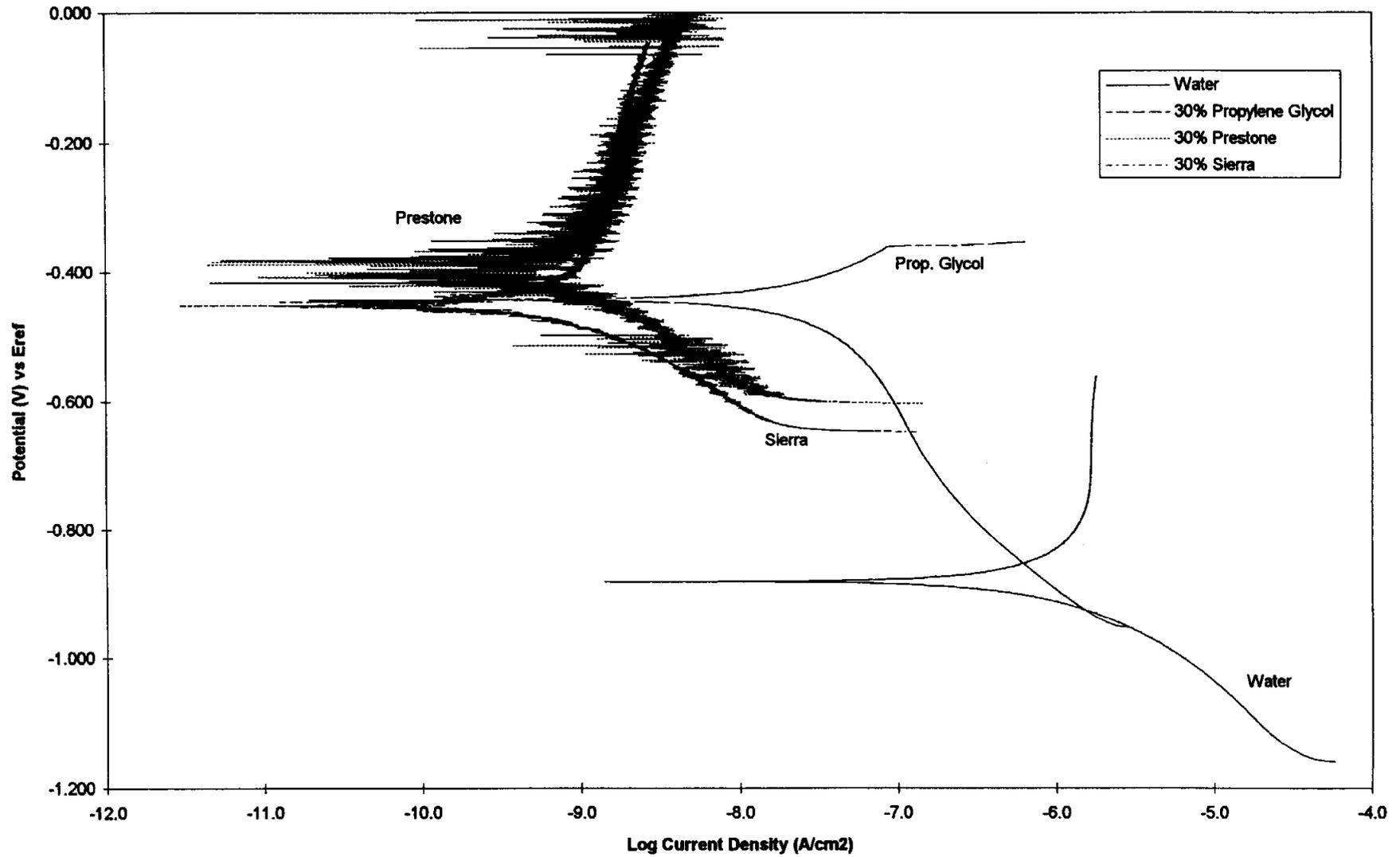


FIGURE 3 - Polarization of Copper 110 in Coolant at 150°F