375
9-20-78

Dr. 525

COO/2934-6

STUDY OF CORROSION AND ITS CONTROL IN ALUMINUM SOLAR COLLECTORS

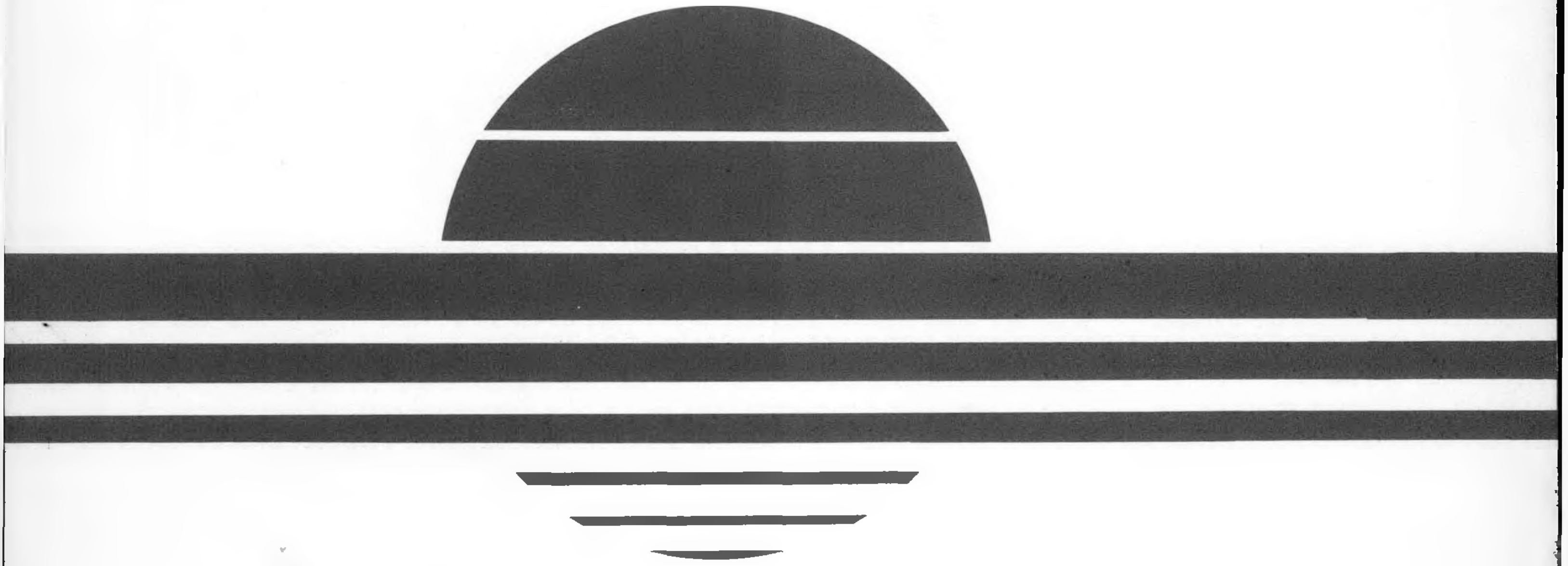
Progress Report, September 1, 1977—March 31, 1978

By
D. Wong
F. H. Cocks
J. Giner

April 1978

Work Performed Under Contract No. EY-76-C-02-2934

Giner, Incorporated
Waltham, Massachusetts



U.S. Department of Energy

MASTER

Solar Energy

NOTICE

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Paper Copy $4.50
Microfiche $3.00

COO/2934-6
Distribution Category UC-59c

STUDY OF CORROSION AND ITS CONTROL IN ALUMINUM SOLAR COLLECTORS

PROGRESS REPORT

For Period September 1, 1977 - March 31, 1978

By:

D. Wong

F. H. Cocks

J. Giner

GINER, INC.
14 Spring Street
Waltham, Massachusetts 02154

APRIL 1978

Prepared for:

Solar Heating and Cooling Research and Development Branch
Conservation and Solar Application
U. S. Department of Energy
Under Contract No. EY-76-C-02-2934

TABLE OF CONTENTS

ABSTRACT

Aluminum solar heat collectors operating on water/glycol heat transfer fluids are potentially attractive but for the critical problem of aluminum corrosion. The goal of this program is to determine the requisite conditions under which such a combination can be safely used.

In Phase I (June 1, 1976 - May 31, 1977) we have developed a non-destructive electrochemical technique (linear polarization resistance method) to determine the overall corrosion rate under various conditions. Pit depth was determined using a quantitative metallographic analysis. The results indicate that aluminum alloys possess *marginal* corrosion resistance in *pure* ethylene glycol solution at temperatures up to 100°C. However, in the presence of common contaminants (e.g. Cu, Fe and NaCl), the corrosion resistance decreases drastically to an intolerable level. It was then concluded that *uninhibited* ethylene glycol solutions most probably will cause catastrophic plant failure when used as a heat transfer medium in an aluminum solar collector system.

Phase II (June 1, 1977 - present) of this program has been geared primarily at the development and evaluation of corrosion inhibitors which will effectively reduce both uniform and localized corrosion. The linear polarization resistance method and the pit depth measurement technique (both developed in Phase I) are used to evaluate the corrosion problems. In addition, a thin foil test method and an aluminum circulation panel (with a heat rejecting surface) were developed and successfully applied to provide added assurance to our major findings. The effects of using chemical scavengers for contaminants were also investigated in this phase of the program.

Furthermore, we also included (a) an investigation of the performance of the inhibited solution at high temperature ($T > 100^{o}C$), (b) an extension of the work to propylene glycol solutions, (c) the verification of the cube root law, and

(d) the determination of the parameter a.

An extensive literature review showed that phosphates, borates, nitrates, silicates and sodium mercaptobenzothiazole are the effective corrosion inhibitors used in ethylene glycol solutions. In Phase II we not only have investigated these inhibitors systematically but have also measured the effects of proprietary formulations. It was found that most inhibitors, whether proprietary or prepared in-house, can reduce the overall corrosion rate to below 1 mpy even with contaminants present *at temperatures below 100°C.* Pitting corrosion is also effectively suppressed. A preferred inhibitor composition range (in g/liter) was found to be (4.5-11.8) $Na_3PO_4 \cdot 12H_2O$, (2.0-2.8) $NaNO_3$, (10.0-12.8) $Na_2B_4O_7 \cdot 5H_2O$, (1.5-3.6) $Na_2SiO_3 \cdot 9H_2O$, and (0.9-5.5) $C_7H_4NS_2Na$.

Inhibitor performance was also evaluated at ∿ 130°C (266°F). Significant pitting corrosion, which had been suppressed at ∿ 100°C, reappears at this temperature. At ∿ 160°C, the overall corrosion rate (derived from weight loss method) becomes intolerable (∿ 3 mpy). Since temperatures above 100°C can be expected in solar collector systems, further improvement of these inhibited ethylene glycol solutions becomes imperative.

The investigation of propylene glycol was carried out because of its low toxicity. We found that corrosion rates are consistently *lower* in uninhibited propylene glycol solutions under all conditions. Because of this encouraging result, a detailed study on aqueous propylene glycol, especially at high temperatures, is certainly warranted.

The parameter a has been determined to be 0.14. The verification of the cube root law and the study of chemically scavenging the contaminants are still in progress.

Upon completion of Phase II (June 30, 1978), results on these tasks are expected to be available. Preliminary results show that serious pitting corrosion occurs in ethylene glycol solution with copper ions at 0.2 ppm. This suggests that a heavy metal ion scavenging technique may not be sufficient to render enough corrosion protection, and a corrosion inhibiting formulation will still have to be incorporated in the system.

I. INTRODUCTION AND SUMMARY

The combined use of aluminum solar heat collector panels with aqueous ethylene (or propylene) glycol solutions as the heat transfer media, appears to have considerable economical advantages vis-á-vis other combinations of collector panel material and heat transfer fluid for a solar thermal energy collector system. These advantages are associated with the low cost, low density, high thermal conductivity, and the ease of fabrication of aluminum alloys, as well as the low cost, ready availability, and the combined anti-freezing, anti-boiling nature of the glycol/water mixtures. However, aluminum and its alloys are known to be susceptible to various types of corrosion in aqueous environment once its protective oxide film is disrupted. Localized pitting corrosion is often to blame for early plant failure, especially with light gauge aluminum structures such as the aluminum solar heat collector panels.

A review of the open literature shows that very little information is available on the corrosion of aluminum in water/glycol mixtures. It is thus imperative to obtain such baseline corrosion information in order to determine the extent of such corrosion problems under conditions directly relevant to the operation of an actual solar collector system. The goal of the program is to determine the requisite conditions for obtaining satisfactory corrosion resistance with the aluminum solar heat collector panels.

The initially proposed program was divided into two phases. The first phase (June 1, 1976 - May 31, 1977) was addressed to the study of the corrosion of aluminum alloys in water/ethylene glycol mixtures in the *absence* of inhibitors. Phase II (June 1, 1977 - June 30, 1978) aims at the development of corrosion control methods.

A. Summary of Phase I

The corrosion rate of aluminum and some selected aluminum alloys in aqueous ethylene glycol solution has been obtained experimentally using a non-destructive electrochemical technique (linear polarization resistance method). Pit depth was assessed via a quantitative metallographic measurement. The scope of this investigation covered the following range of conditions:

(1) four different aluminum alloys (i.e. 99.9% pure, 1100, 3003 and 3004 series aluminum);

(2) $\sim 25 - \sim 100^{\circ}C$ ($\sim 75 - \sim 210^{\circ}F$)

(3) stagnant solutions, laminar and turbulent flows;

(4) under N_2 and under air;

(5) presence of contaminants (e.g. Cl^-, Cu^{+2} and Fe^{+3} ions); and

(6) effects of ethylene glycol decomposition products.

In addition, the extent of galvanic attack and the susceptibility to stress corrosion cracking were also investigated for the aluminum ethylene glycol solution combination.

These results can be summarized as follows:

1. All four aluminum alloy compositions tested showed satisfactory corrosion resistance to uniform corrosion and *marginal* tolerance to pitting corrosion in *pure* aqueous ethylene glycol solution.

2. Cl^-, Fe^{+3} or Cu^{+2}, when present at 200 ppm in solution, Cu^{+2} and Cl^- cause severe pitting damage, while Fe^{+3} accelerates uniform attack drastically.

3. The temperature dependence of the measured corrosion rate is relatively small, with $\Delta H < 5$ Kcal/mole.

4. The presence of dissolved oxygen was not found to increase corrosion damage significantly. Hydrodynamic flow conditions and ethylene glycol decomposition products did not seem to affect the measured corrosion rates.

5. Stress corrosion cracking in aluminum solar collector panels made of relatively low yield strength alloys (e.g. 1100 and 3003 series aluminum) did not appear to be a problem.

6. Galvanic attack on aluminum due to direct electrical contact with copper was found to be attributed to localized deposition corrosion. The corrosion rate depends on the anode (aluminum) to cathode (copper) surface area ratio, as well as the electrical conductivity of the solution. In *pure* ethylene glycol solution ($\sigma = 3.0 \times 10^{-6}$ mho/cm) such attack is negligible, however, in the presence of impurities, the corrosion rate greatly increases and damage would be rapid and severe.

7. An aluminum alloy galvanic series in aqueous ethylene glycol solutions at 35% by volume has been established.

B. Summary of Work Performed in Phase II

During this reporting period, we have completed the study of corrosion behavior of aluminum in both *pure* and *contaminated* propylene glycol solutions. Pure propylene glycol solutions were found to be *less* corrosive to aluminum alloys. This is most probably attributed to the high solution pH which were measured at between 8 and 9. The presence of chloride and copper ions causes pitting corrosion, and ferric ions accelerate a more uniform type of attack on aluminum. The results are very similar to what we found for aluminum in water/ethylene glycol mixtures. Although the extent of the corrosion problems in these cases were noted to be *one order of magnitude lower* than the ones in ethylene glycol solutions, the corrosion resistance of aluminum is still *not* sufficient for any light gauge aluminum structure to survive a reasonable duration.

Verification of the cube root pit growth law is still in progress. Results to date indicate the cube root law seems to be obeyed within experimental error. The parameter a was determined to be 0.14.

We have prepared and evaluated two inhibited ethylene glycol solutions using the inhibitors developed for automotive cooling systems. Nitrates, silicates, borates, phosphates and sodium mercaptobenzothiazole are used as corrosion inhibitors in these solutions. The pH of the solution is usually adjusted to more alkaline to offset any detrimental effects from ethylene glycol decomposition products. This type of inhibited solution was found to provide fairly satisfactory corrosion protection to aluminum alloys, even with deleterious contaminants present, at temperatures up to ∿ 100°C (∿ 210°F). At higher temperatures (up to ∿ 160°C) the corrosion rate was found to increase to ∿ 3 mpy, which is considered intolerable for light gauge aluminum structures.

Inhibitor formulas developed specifically for aluminum solar systems were also obtained and tested. In addition, an inhibitor concentrate was also made available for evaluation. Results showed that two out of the three proprietary formulations tested failed to protect aluminum from severe pitting attack. Only one was found to reduce the corrosion problems as effectively as the inhibited automotive coolants. However, at high temperatures a similar acceleration in aluminum corrosion rate occurs in this commercial solar collector heat transfer solution. In conclusion, the inhibitors developed so far are effective, while the solar collector panel fluid is in circulation (at temperatures below ∿ 100°C). However, corrosion rate will reach a higher level while the collector system is at stagnation ($T > 100^{\circ}C$). Further improvements are needed to develop inhibitors which are effective at higher operating temperatures ($T > 100^{\circ}C$). The lifetimes of such inhibited solutions will also have to be determined.

We have also successfully applied thin foil samples to verify the major findings described before. Some preliminary experiments were performed to determine the effect of copper ion concentration on the pitting of aluminum in ethylene glycol solutions. Severe pitting was still observed, even at a copper ion concentration as low as 0.2 ppm. It indicates that even with heavy metal ions scavenging methods incorporated in the solar heat collector system, inhibitors will have to be used.

During the remainder of Phase II, work will be scheduled to (a) determine the effects of chemical scavengers for contaminants, (b) complete the verification of cube root law, (c) develop inhibitors which can be safely used in propylene glycol solutions, and (d) improve the inhibitor performance at operating temperatures above 100°C.

II. EXPERIMENTAL METHODS

A. Linear Polarization Resistance Measurement

The method that is being used to determine the overall corrosion rate is an electrochemical measurement of linear polarization resistance. This is a non-destructive and sensitive method for determining low corrosion rates than either weight loss or gas collection methods. Corrosion processes are mixed electrode reactions with the corrosion potential determined by both an anodic reaction (metal oxidation) and a cathodic reduction reaction on the metal surface. In the specific case of aluminum corrosion, the anodic reaction is aluminum dissolution, and the cathodic reaction is water reduction to hydrogen, in total absence of oxygen or oxygen reduction when oxygen is present in sufficient amounts.

As a consequence of the action of the anodic and cathodic reactions, the corrosion potential adopts a value which is more positive than the thermodynamic potential of the metal oxidation reaction and more negative than that of the cathodic reduction reaction. In the case of aluminum corrosion, the potential is slightly more negative than the hydrogen electrode potential in de-aerated solutions and considerably more positive than this potential in aerated solutions.

The measurements are performed in a three-electrode cell containing the glycol/water solution. A small amount of current (sufficient to polarize the aluminum to a maximum of 10 mV about its corrosion potential) is passed between the aluminum and a counter electrode of pure graphite. The potential of the aluminum sample is measured versus a reference electrode which can be any electrode that remains constant during the measurement and does not contaminate the solution.

A plot of applied current versus potential difference, at low polarization, yields a straight line, the slop of which ($\Delta E/\Delta i$) is defined as the linear polarization resistance. The overall corrosion current density can then be derived from the Stern-Geary equation(1):

$$i_{corr} = \frac{\beta_a \beta_c}{2.3 \left(\frac{\Delta E}{\Delta i}\right) (\beta_a + \beta_c)} \qquad (1)$$

i_{corr}, the corrosion current density, can then be converted to corrosion penetration rate in mils/year or other convenient units. The Tafel parameters, β_a and β_c, are the slopes of the logarithmic local anodic and cathodic polarization curves, respectively. The values of β_a and β_c can also be determined experimentally using the same set-up. This electrochemical method of measuring the corrosion rate has been used successfully by several investigators to study aluminum corrosion in various media(2) including aqueous ethylene glycol solutions(3,4). The derivation(5) and validity(6) of the Stern-Geary equation have been fully discussed and reported in previous reports.

Similar sample and cell configurations as used in Phase I are adopted here. The same multi-station rotating electrode system is used to generate corrosion data under different flow conditions. All aluminum samples are annealed according to Aluminum Association specifications to relieve machining stress and polished with 320 and 600 grit SiC paper.

The test period for all samples is at least seven days. Daily linear polarization resistance measurement is made for all samples. The linear polarization resistance is found to increase during the first few days until finally a stabilized value is reached after the establishment of steady state conditions at the metal/solution interface(3). This technique is not only used to generate baseline corrosion data but also to evaluate the effectiveness of the various inhibitors.

B. Determination of Tafel Slopes

The Tafel parameters, β_a and β_c, are directly determined experimentally rather than estimated from the literature. This measurement is similar to the linear polarization resistance determination. The difference is in polarizing the working electrode beyond the linear region up to about 100 mV more anodic or cathodic than the corrosion potential. This overvoltage is then plotted against the current density on a semilog scale. The two slopes of the curves obtained in the most anodic and cathodic regions (Tafel regions) are β_a and β_c, respectively.

C. Measurement of Pitting Corrosion

The pitting corrosion of selected aluminum alloys has been studied by measuring the maximum pit depth and pit density on each sample used in the electrochemical corrosion measurement under various conditions. The pit growth constant k is determined by the following equation(7):

$$D = k\ t^{1/3} \qquad (2)$$

where D is the measured pit depth and t is the exposure time.

Pitting analysis is done by a quantitative metallographic examination of the surface of the aluminum sample after timed exposure to the ethylene glycol/water solution under various conditions of temperature, hydrodynamic flow, gas atmosphere and contaminants. At high magnification (500X) the instrument is first focused on the surface of the aluminum and then on the bottom of various pits to establish pit depth. Pit density and diameter are determined at the same time. Under flow conditions, the mounted samples for linear polarization resistance measurements are used for pitting analysis also. Larger surface area samples are used for stagnant cases.

Since pit depth follows a Gaussian distribution with respect to exposed wetted surface area, the following equation is adopted to estimate the maximum pit depth expected in a real plant with wetted surface of A times larger than that of a laboratory sample(8).

$$p = k\ t^{1/3}\ A^{a} \qquad (3)$$

Where p is the maximum probable pit penetration depth to be found on the exposed surface of such a plant, k and t are the same as defined in Eq. (2), and a is a parameter which has been determined experimentally. During the first quarter of

Phase II, we have exposed aluminum sheet samples of relatively large surface area in corrosive aqueous ethylene glycol environment to induce severe pitting corrosion. The exposed surface was then divided arbitrarily into N equal sections. The maximum pit depth D for each section was measured. The maximum and minimum values of D are designated as D(max) and D(min), respectively. The parameter a is then derived from:

$$a = \frac{\log \left[D(\max)/D(\min)\right]}{\log N} \qquad (4)$$

D. High Temperature Performance Test

The inhibited ethylene (or propylene) glycol solutions, with or without added contaminants, are also subject to a high temperature performance test at ∿ 160°C (320°F). These solutions are contained in glass beakers which are placed in an electric pressure cooker with a thermostatic temperature control. Aluminum samples are also immersed in these solutions to generate corrosion data at this temperature via the conventional weight loss technique. The exposure period is normally scheduled for 10 days. Both the change in the solution pH (before and after the high temperature test) and the weight loss are used to evaluate the performance of each inhibitor formula. Pitting measurement is also made on samples with pits after the exposure.

E. Circulation Panel

An aluminum circulation panel was designed and constructed to simulate the operation of an actual aluminum solar heat collector panel. It consists of an aluminum backing panel, together with an inert transparent covering plate and a Teflon flow chamber. The aluminum panel is heated from behind, and the heat transfer fluid is circulated through the flow chamber to cool down a heat rejecting surface. We will be able to perform: (a) linear polarization resistance measurement, (b) pit depth and density analysis, and (c) time lapse photography with heat transfer fluid in circulation. This panel will be used primarily to double check the effectiveness of various inhibitors developed in this program.

F. Thin Foil Method

Thin foils of different aluminum alloys are commercially available at various thicknesses. Aluminum samples made of thin foil provide accelerated (yet undistorted) experimental results. In some cases pitting perforation can be visually detected in a matter of days or even hours. Perforation time is obtained from visual examination at regular time intervals. In addition, the linear polarization resistance, weight loss and/or the ohmic resistance of the thin foil samples can be measured to determine the extent of corrosion problems under various conditions.

This newly developed corrosion measurement technique is also used to verify the major findings obtained via other methods adopted in the program.

III. RESULTS AND DISCUSSION

A. Task I - Laboratory Study of Corrosion of Aluminum Alloys in Propylene Glycol/Water Mixtures

It was decided at an earlier stage to devote part of the effort of this second phase of the program to the further understanding of aluminum corrosion in glycol/water solutions under various conditions relevant to the operation of a solar thermal energy collector system. The first target was to determine the corrosion characteristics of aluminum and its alloys in *propylene* glycol/water solutions. This heat transfer medium may be more desirable than ethylene glycol due to the fact that propylene glycol is far less toxic while still providing similar anti-freezing and anti-boiling protection. However, similar corrosion problems are also expected to be encounted for aluminum in propylene glycol solutions.

In addition to the gathering of baseline corrosion data for the aluminum in propylene glycol, the acquisition of extended baseline corrosion data for aluminum alloys in ethylene glycol solutions is also included in this task. Especially, we are interested in the corrosion behavior of aluminum alloys in more concentrated ethylene glycol solutions (up to 85 vol %) at higher operating temperatures (higher than 100°C).

The results are presented as follows:

1. Baseline Corrosion Behavior of Aluminum Alloys in Pure Propylene Glycol Solutions

Linear polarization resistance measurements of 1100 series aluminum samples in a 50 vol % propylene glycol solution were made under laminar flow conditions within a temperature range from ∿ 25 to 100°C. At ambient temperature the pH and the electrical conductivity of this solution were measured to be 8.49 and 5.0×10^{-7} moh/cm, respectively. The Tafel slopes, β_a and β_c, were also determined experimentally. $\beta_a\beta_c/(\beta_a + \beta_c)$ was found to be ∿ 0.07 V/decade under all conditions. All these results are shown in Table I. The corrosion rates are fairly low and only slightly temperature dependent with an activation energy estimated at ∿ 4 Kcal/mole.

All aluminum samples have been examined for signs of pitting corrosion. Not a single pit was observed on any of these samples. 1100 and 3003 series aluminum sheet samples with total exposure area of more than 200 cm^2 were also exposed to a stagnant pure 50 vol % propylene glycol solution at 100°C in a separate experiment. Again, pitting was not found to be a problem.

These results strongly lead to the conclusion that aluminum alloys are indeed *more corrosion resistant* in the propylene glycol/water medium. Even pitting corrosion was not observed within the range of the experimental conditions. This is most probably due to the high pH of propylene glycol solutions, since aluminum alloys are known to be more corrosion resistant (especially to pitting attack) in slightly alkaline environment(9).

2. Corrosion Characteristics of Aluminum Alloys in Contaminated Propylene Glycol/Water Mixtures

The linear polarization resistance of aluminum alloys in 50 vol % contaminated propylene glycol solutions have also been measured experimentally, and the results are reported in Table II. Once again, $\beta_a\beta_c/(\beta_a + \beta_c)$ was found to be ∿ 0.07 V/decade under all conditions. As we expected, the presence of chloride or copper ions (at 200 ppm) in propylene glycol solutions caused a drastic decrease in the corrosion resistance. Severe pitting was observed (especially with Cu^{+2} present). Fe^{+3} ions (at 200 ppm) were found to accelerate the uniform corrosion rate up to ∿ 10 mils per year. The simultaneous presence of these three species in solar collectors will lead to rapid plant failure. The corrosion rate was again found to be slightly temperature dependent with an activation energy estimated at less than 5 Kcal/mole.

TABLE I

LINEAR POLARIZATION RESISTANCE OF ALUMINUM ALLOYS IN PURE 50 VOL % PROPYLENE GLYCOL SOLUTIONS

Temp (^{o}C)	Alloy	$\frac{\Delta E}{\Delta i}$ (Ω/cm^2)	R_{corr} (mpy)
100	3003	3.3×10^5	0.039
100	1100	2.2×10^5	0.059
75	1100	5.0×10^5	0.026
25	1100	9.3×10^5	0.014

TABLE II

LINEAR POLARIZATION RESISTANCE OF ALUMINUM ALLOYS IN 50 VOL % PROPYLENE GLYCOL SOLUTIONS WITH CONTAMINANTS

Contaminants*	Alloy	Temp($^\circ$C)	Flow	$\frac{\Delta E}{\Delta i}$ (Ω/cm^2)	R_{corr}(mpy)
Cl^-	1100	100	laminar	4.1×10^3	3.2
	1100	75	laminar	7.0×10^3	1.9
	1100	25	laminar	2.2×10^5	0.06
Cu^{+2}	1100	100	laminar	1.0×10^4	1.3
	3003	100	laminar	1.6×10^4	0.8
Fe^{+3}	1100	100	laminar	1.8×10^3	7.2
Cu^{+2}+Fe^{+3}+Cl^-	1100	100	laminar	8.0×10^2	16
	3003	100	laminar	1.2×10^3	11
	1100	100	stagnant	5.7×10^2	23
	1100	75	stagnant	6.2×10^2	21
	1100	25	stagnant	3.3×10^3	3.9

---

* at 200 ppm each.

The samples used in the linear polarization resistance experiment were then examined metallographically to determine pit depth. Additional pitting data were generated by exposing aluminum samples (2" x 2" sheets) in stagnant solutions. The maximum pit depth D was measured, and the pit growth constant k and probable pit penetration depth p on a life size plant (with wetted surface area of 1.5×10^5 cm^2) in 20 years were determined. All these results are shown in Table III. p serves as the parameter which determines the relative severity of pitting attack among all cases studied in this work.

From Table III we noted that both Cl^- and Cu^{+2} are mainly responsible for severe pitting corrosion in these 50 vol % propylene glycol solutions. As we increase the propylene glycol concentration from 50 to 85 vol %, pitting damage is seen to decrease by one order of magnitude. This added corrosion resistance may be attributed to the higher resistivity of the electrolyte. Based on the results obtained so far, we noted:

(i) Chloride and copper ions induce severe pitting on aluminum while ferric ions are responsible for the drastic acceleration in uniform attack These effects are very similar to the ones observed for the aluminum in ethylene glycol solutions.

(ii) The corrosion resistance of aluminum was found to be *higher* (by one order of magnitude) in propylene glycol/water mixtures. This is probably due to the higher pH of the propylene glycol solution. However, it is still not sufficient for any light gauge aluminum structure to survive a reasonable period without the incorporation of proper corrosion control methods.

(iii) Since pitting corrosion was found to be less severe in more concentrated propylene glycol solutions, heat transfer fluids used in solar heat collector systems should contain more than 50 vol % propylene glycol.

3. Extended Baseline Information on Aluminum Corrosion in Contaminated Ethylene Glycol Solutions

Additional baseline corrosion information on aluminum and its alloys in ethylene glycol solutions has been obtained in the second phase of the program.

TABLE III

PITTING CORROSION DATA OF ALUMINUM ALLOYS IN CONTAMINATED PROPYLENE GLYCOL SOLUTIONS

Solution Composition	Alloy	Temp (^{o}C)	Flow	Sample Area (cm^2)	D_{max} (μ)	K(μ/day$^{1/3}$)	P*(mils)
50% P.G. + Cl^- (200 ppm)	1100	100	laminar	2.36	230	110	400
	1100	75	"	1.18	200	93	370
	1100	25	"	1.18	160	74	290
50% P.G. + Cu^{+2} (200 ppm)	1100	100	"	2.36	70	33	250
	3003	100	"	1.18	40	21	83
50% P.G. + Fe^{+3} (200 ppm)	1100	100	"	2.36	0	0	0
50% P.G. + Cu^{+2} + Fe^{+3} + Cl^- (200 ppm each)	1100	100	"	2.36	380	170	160
	3003	100	"	1.18	280	150	590
	1100	100	stagnant	104.4	260	120	250
	1100	75	"	1.18	280	130	510
	1100	25	"	1.18	190	88	350
	3003	100	"	103.2	120	83	180
85% P.G. + Cu^{+2} (200 ppm)	1100	130	"	103.2	10	5.2	11
	3003	130	"	103.2	10	5.2	11
85% P.G. + Cu^{+2} + Fe^{+3} + Cl^- (200 ppm each)	1100	130	"	103.2	60	31	66
	3003	130	"	103.2	65	34	72

---

* The calculations were made based on a plant with wetted surface area of 1.5×10^5 cm^2 after 20 years of operation.

Basically, corrosion data were generated in more concentrated ethylene glycol solutions at temperatures higher than 100°C. In addition, we have determined the value of _a_ and set up experiments to verify the cube root pit growth law adopted in this program.

During this reporting period, we have gathered pitting data to determine the validity of the cube root pit growth law. Two simultaneous experiments were set up with several sets of aluminum samples exposed to 85 vol % ethylene glycol solutions with 200 ppm $CuSO_4$ and $CuSO_4$, NaCl and $Fe_2(SO_4)_3$ at 200 ppm each added. The solution temperature was set at 130°C. One set of samples was taken out at the end of a certain time period for pitting analysis. We expect to obtain pitting data on samples immersed for 1, 2, 3, 4, 6, 8, 12, 20 and 32 weeks. The entire experiment will be completed by May 1978, and the results to date are shown in Table IV. The results indicate that the cube root growth law is capable of predicting the propagation of pit fairly reasonably. Pitting of 3003 series aluminum alloys in 85 vol % ethylene glycol with 200 ppm $CuSO_4$ obeys the cube root pit growth law especially well. This experiment is still in progress, and complete results will be available in May 1978. The parameter _a_ was determined during the first quarter of Phase II (June 1, 1977 - August 31, 1977). A value of 0.14 for _a_ was obtained experimentally.

B. Task II - Development of Effective Inhibitors for Aluminum in Pure and Contaminated Glycol/Water Mixtures

Based on the results to date, the use of *uninhibited* glycol/water mixtures in aluminum solar heat collectors will definitely cause serious corrosion problems, especially with chloride and heavy metal ions present. It is thus mandatory to develop corrosion control and prevention methods to protect such systems. Since ethylene glycol based antifreeze has been used successfully as an automotive engine coolant for over half a century, many corrosion inhibitors have been developed to protect the system within its operating conditions. A solar heat collector system

TABLE IV

VERIFICATION OF CUBE ROOT LAW

	85% E.G. + Cu^{+2} (200 ppm)				85% E.G. + Cu^{+2} + Cl^{-} + Fe^{+3} (200 ppm ea.)			
	1100 alloy		3003 alloy		1100 alloy		3003 alloy	
Days	D(μ)	K(μ/day$^{1/3}$)	D(μ)	K(μ/day$^{1/3}$)	D(μ)	K(μ/day$^{1/3}$)	D(μ)	K(μ/day$^{1/3}$)
7	95	50	100	52	100	52	100	52
14	120	50	130	54	120	50	120	50
21	125	45	120	44	85	31	105	38
28	170	56	155	51	230	76	190	63
42	280	81	170	49	320	92	200	56
56	270	74	205	56	290	80	225	62
84	-	-	-	-	180	41	160	37

is, in many ways, analogous to an automotive cooling system which consists of dissimilar metals exposed constantly to the heat transfer solution. The major differences are that the continuous operating hours for solar collectors are much longer than in automotive application, and the collector panel fluid may be at higher temperature (more than 150°C) at stagnation.

Through an extensive literature search, we found that phosphates, borates, nitrates, silicates and sodium mercaptobenzothiazole (NaMBT) are the common corrosion inhibitors(10,11) in the automotive coolants, although the exact formulas are invariably proprietary. The functions of each inhibiting agent and two compositions of inhibitor formulations (Formulas I and II) prepared and examined in this program are shown in Table V. The inhibitors used also render protections to copper and steel since most solar collector systems come with components made of these metals. Furthermore, the decrease of corrosion of copper and steel will consequently reduce the corrosiveness of the solution to the more active aluminum collector panels.

1. Preparation of Inhibited Ethylene Glycol Solutions

Two inhibited ethylene glycol solutions (Formulas I and II) were prepared according to the compositions shown in Table V. It is important that proper mixing procedures be followed to minimize the formation of insolubles. A commonly adopted procedure(11) is to dissolve the borate in ethylene glycol with stirring; then dissolve the nitrate, silicate and phosphate in a separate portion of distilled water with mild heating before adding to the glycol borate solution; and finally, add the NaMBT solution. The water content should be kept below 2 wt %.

The pH's and electrical conductivities of 85 vol % of both inhibited ethylene glycol solutions (Formulas I and II) were measured at ambient temperatures, and the results are also shown in Table V. Sodium hydroxide was added to Formula II primarily to adjust the solution pH to more alkaline in order to offset the effect of possible organic acid formation from ethylene glycol oxidation.

TABLE V

FUNCTIONS AND CONCENTRATIONS OF CORROSION INHIBITORS USED IN ETHYLENE GLYCOL SOLUTIONS

Inhibitor	Concentration (g/liter) Formula I	 Formula II	Function
Sodium Orthophosphate $Na_3PO_4 \cdot 12\ H_2O$	4.5	4.5	Protects aluminum and steel
Sodium Nitrate $NaNO_3$	2.5	2.0	Protects aluminum and iron
Sodium Tetraborate $Na_2B_4O_7 \cdot 5\ H_2O$	11.2	10.0	Strong buffering agent also protects steel
Sodium Meta Silicate $Na_2SiO_3 \cdot 9H_2O$	2.0	1.5	Protects all metals
Sodium Mercaptobenzothiazole $C_7H_4NS_2Na$ 50% solution	1.8	5.5	Protects brass and copper
Sodium Hydroxide NaOH		2.0	Adjusts the solution pH
	pH = 6.86 $\sigma = 1.7 \times 10^{-3}$ mho/cm	pH = 11.0 $\sigma = 2.5 \times 10^{-3}$ mho/cm	

In addition to the two inhibited ethylene glycol solutions prepared in the laboratory, several commercially available coolants were also obtained and evaluated experimentally. This includes two inhibited automotive coolants (A1 and A2), two inhibited heat transfer fluids specifically designed for aluminum solar collectors (S1 and S2), and an inhibitor concentrate (C). A1 and A2 contain more than 95 wt % ethylene glycol. Inhibitor S1 is an inhibited 50 vol % ethylene glycol solution, while S2 is a 50 vol % propylene glycol based inhibited heat transfer fluid. Inhibitor C is an aluminum inhibitor concentrate which can be added to pure ethylene glycol at concentrations ranging from 0.1 to 1.0 wt %.

2. Aluminum Corrosion in Inhibited Glycol Solutions

Aluminum corrosion characteristics have been studied in these inhibited glycol/water mixtures in the absence of any deleterious species using both the linear polarization resistance and pitting analysis methods at temperatures up to ∿ 100°C (∿ 210°F). Furthermore, each inhibited solution was also subject to a high temperature performance test at temperatures up to ∿ 160°C (320°F).

a. Linear Polarization Resistance

The linear polarization resistance measurements were performed at ∿ 100°C (∿ 210°F) under laminar flow conditions. These results are shown in Table VI. The pH and electrical conductivity of each inhibited glycol solution is also reported. In general, we found that the inhibited solutions are much more conductive (by about three orders of magnitude) than the pure glycol/water mixtures. In most cases, the pH of the inhibited solution is adjusted to slightly alkaline. The measured corrosion rates shown in Table VI are actually *higher* than the ones obtained in the pure uninhibited solutions. However, most of the rates were found to be within the tolerable range (less than 1 mpy) with inhibitor S1 being the only exception. This increase is most probably due to the high solution conductivity. Inhibitor Formula I was found to form a gel-like layer around the exposed aluminum sample. This film probably provides corrosion protection; however, the same film

TABLE VI

LINEAR POLARIZATION RESISTANCE OF ALUMINUM ALLOYS IN INHIBITED AQUEOUS GLYCOL SOLUTIONS UNDER LAMINAR FLOW CONDITIONS

Solution	pH$^+$	σ(mho/cm)$^+$	Alloy	Temp($^\circ$C)	$\frac{\Delta E}{\Delta i}$ (Ω/cm^2)	R$^*_{corr}$(mpy)
35 vol% Inhibitor A1	10.0	$2.1\text{x}10^{-3}$	3003	100	$9.0\text{x}10^4$	0.32
			1100	100	$1.6\text{x}10^5$	0.19
			1100	75	$1.9\text{x}10^5$	0.16
			1100	25	$4.6\text{x}10^5$	0.07
50 vol % Inhibitor A2	8.85	$3.1\text{x}10^{-3}$	3003	100	$1.0\text{x}10^5$	0.30
			1100	100	$1.0\text{x}10^5$	0.30
85 vol % Formula I	6.86	$1.7\text{x}10^{-3}$	3003	100	$7.5\text{x}10^4$	0.40
			1100	100	$4.0\text{x}10^4$	0.74
50 vol % Formula II	10.9	$3.0\text{x}10^{-3}$	1100	100	$1.5\text{x}10^5$	0.20
			1100	50	$1.8\text{x}10^5$	0.16
			1100	25	$5.5\text{x}10^5$	0.05
Inhibitor S1	7.6	$7.4\text{x}10^{-4}$	1100	100	$2.5\text{x}10^4$	1.2
Inhibitor S2	7.3	$4.6\text{x}10^{-4}$	1100	100	$2.7\text{x}10^5$	0.05

---

* $\beta_a \beta_c/(\beta_a + \beta_c)$ was assumed at 0.16 V/decade and 0.07 V/decade for ethylene glycol and propylene glycol based solution, respectively.

$^+$Measured at ambient temperature.

most certainly will hinder the heat transfer efficiency and may eventually block the fluid passage.

b. Pitting Corrosion

Rotating samples used in the linear polarization resistance experiments were examined for pitting corrosion. In addition, larger aluminum samples (2" x 2" sheets) were immersed in stagnant solutions to induce pits at temperatures above 100°C. In most cases pitting corrosion was not found to be of any concern. The only exception is Inhibitor C, which was found to be ineffective to protect aluminum from pitting corrosion. Pits as deep as 90μ were found on both 1100 and 3003 series aluminum samples after 4 weeks at 110°C. The relevant data are shown in Table VII. The probable penetration depth $\underline{p}$ on a lifesize plant with a 1.5×10^5 cm^2 wetted surface area in 20 years is estimated to be ∿ 60 mils, which is intolerable.

Based on these results, most inhibited glycol/water solutions are effective in preventing aluminum from pitting attack, although the measured overall corrosion rates were found to be higher than the ones obtained in pure water/glycol mixture. Inhibitor Formula I and Inhibitor C do not seem to perform as well as the other solutions examined in this work.

c. High Temperature Performance Test

The inhibited glycol/water solutions were tested in a pressure cooker for their performance at ∿160°C (320°F). The weight loss of the aluminum samples and the changes of solution pH (before and after the exposures) are reported in Table VIII. The pH changes of solutions without aluminum samples were also measured.

The solution pH was found to decrease as a result of the high temperature exposure. A sharp drop of as much as 5 pH units was observed for solutions with Inhibitor C. The presence of aluminum samples in the solution resulted in an

TABLE VII

PITTING CORROSION OF ALUMINUM IN INHIBITED ETHYLENE GLYCOL SOLUTION

(4 weeks, 110°C)

Solution	Alloy	Sample Area (cm^2)	D(μ)	K(μ/day$^{1/3}$)	P(mils)
50% E.G. + 0.05% Inhibitor C	1100	103.2	85	28	59
	3003	103.2	90	30	63

TABLE VIII

HIGH TEMPERATURE PERFORMANCE OF INHIBITED GLYCOL SOLUTIONS (at 160°C)

Solution	Aluminum Sample	pH Before	pH After	Duration (days)	ΔW(mg)	R^*_{corr}(mpy)
100% Inhibitor A1	w/o	10.0	9.4	11	-	-
	w	10.0	8.5	11	16.9	3.1
100% Formula II	w/o	11.1	7.3	11	-	-
	w	11.1	7.2	11	16.1	3.0
Inhibitor S1	w/o	7.6	7.1	7	-	-
	w	7.6	7.1	7	10.3	3.5
E.G. + .1% Inhibitor C	w/o	8.1	2.5	10	-	-
	w	8.1	2.5	10	13.7	2.8
E.G. + 1% Inhibitor C	w/o	7.8	2.6	10	-	-
	w	7.8	2.4	10	9.3	1.9

---

* obtained from weight loss data.

additional decrease in the pH, however, this effect is minimal. We also noted that the corrosion rates are at ∿ 3 mpy which is almost one order of magnitude higher than the ones obtained at 100°C. This surge of corrosion rate indicates clearly that the corrosion inhibition mechanism is failing at this elevated temperature. Pitting was still found not to be a problem for most inhibitors tested in the program (with the sole exception of Inhibitor C).

3. Effects of Inhibitors in Glycol/Water Mixtures with Deleterious Contaminants

The performance of the inhibited glycol mixtures in the presence of contaminants has been determined as follows:

a. Linear Polarization Resistance Method

We have obtained the linear polarization resistance of 1100 and 3003 series aluminum alloys in various inhibited glycol solutions with different added contaminants. Most of the measurements were performed under laminar flow conditions within a temperature range from ∿25 to ∿100°C. The results are shown in Table 9. We noted that most of these inhibited solutions rendered excellent corrosion protection within the range of experimental conditions ($T < 100°C$). These inhibitors effectively reduced the corrosion attack on aluminum to less than 1 mpy for most cases, even when all three major contaminants are present. However, we did observe the formation of insoluble precipitates in most solutions examined in this work. This effect most probably will hinder the heat transfer properties and may even cause crevice corrosion in solar collectors. Finally, we must emphasize that the inhibitor level must be maintained. Depletion of inhibitors will result in a rapid surge of corrosion attack which leads to catastrophic plant failure.

b. Pitting Corrosion Data

All samples used in the linear polarization resistance measurements have been subject to metallographic pitting examination. In addition, larger

TABLE IX

LINEAR POLARIZATION RESISTANCE OF ALUMINUM IN INHIBITED GLYCOL SOLUTIONS WITH CONTAMINANTS

Additives*	Base Solution+	Alloy	Temp(^{o}C)	Flow	$\frac{\Delta E}{\Delta i}(\Omega/cm^2)$	R_{corr}(mpy)
Cl^-	35% Inhibitor A1	1100	100	laminar	$6.4x10^4$	0.46
	50% Inhibitor A1	1100	100	laminar	$1.2x10^5$	0.25
	50% Inhibitor A2	1100	100	laminar	$5.0x10^4$	0.59
		3003	100	laminar	$4.3x10^4$	0.69
	50% Formula II	1100	100	laminar	$1.2x10^5$	0.25
		1100	75	laminar	$1.7x10^5$	0.17
		1100	25	laminar	$2.2x10^5$	0.13
Cu^{+2}	35% Inhibitor A1	1100	100	laminar	$4.1x10^4$	0.72
	50% Inhibitor A2	1100	100	laminar	$4.5x10^4$	0.66
	50% Formula II	1100	100	laminar	$7.0x10^4$	0.42
Fe^{+3}	35% Inhibitor A1	1100	100	laminar	$1.0x10^5$	0.30
Cu^{+2}+Fe^{+3}+Cl^-	50% Inhibitor A2	1100	100	stagnant	$5.9x10^4$	0.50
	85% Formula I	1100	100	laminar	$7.6x10^4$	0.39
		3003	100	laminar	$5.2x10^4$	0.57
	50% Formula II	1100	100	stagnant	$1.7x10^4$	1.7
		1100	75	stagnant	$4.0x10^4$	0.74
		1100	25	stagnant	$6.0x10^4$	0.49
	Inhibitor S1	1100	100	laminar	$4.0x10^4$	0.74
	Inhibitor S2	1100	100	laminar	$2.0x10^4$	0.65

---

*At 200 ppm each added species

+Percent by volume.

surface area aluminum sheet samples (2" x 2") were exposed to these contaminated fluids at higher temperatures (up to 130°C) under stagnant conditions for up to 4 weeks to generate more pitting data. We did not see any pits on samples exposed to Inhibitors A1, A2, S1 and Formula II, even when chloride and heavy metal ions were simultaneously present at 200 ppm each. However, pitting was observed on aluminum samples in Inhibitor S2 and in a 50% ethylene glycol solution with 0.05% Inhibitor C at 110°C. The results, which are shown in Table X, clearly indicate that these two inhibited glycol solutions are unacceptable.

c. High Temperature Performance Test

Aluminum samples (1" x 2") were immersed in various *inhibited* ethylene glycol solutions with contaminants at very high temperature (160°C). Ethylene glycol decomposition and possible inhibitor degradation may occur and cause rapid increases in corrosion. A weight loss method was used to determine the extent of corrosion problems. The pH of each solution was measured before and after the exposure. A specific contaminant composition with $CuSO_4$, $Fe_2(SO_4)_3$ and NaCl at 200 ppm each was chosen in this investigation. At this temperature (160°C) corrosion rates were measured at over 3 mpy. Pitting corrosion, which was suppressed at 100°C, began to reappear. The results are summarized in Table XI.

In conclusion, most of the inhibitors developed for the automotive cooling system provide sufficient corrosion protection to aluminum alloys in solar collector applications at temperatures up to ∿ 100°C. Three of the tested inhibited solutions were found to be unsatisfactory. Inhibitor Formula I forms gel-like film which is undesirable. Inhibitors C and S2 are unacceptable because they fail to protect aluminum from pitting corrosion. At higher operating temperature (160°C), the overall corrosion rate surged to an intolerable level (above 3 mpy). Pitting corrosion reappeared in most cases at this temperature. More work needs to be directed to the understanding of the inhibitor breakdown at such high temperatures.

TABLE X

PITTING CORROSION OF ALUMINUM IN INHIBITED GLYCOL/WATER SOLUTIONS WITH CONTAMINANTS

(exposed sample area = 103.2 cm^2, 130°C, 4 weeks)

Solution	Additive(s)*	Alloy	D(μ)	K(μ/day$^{1/3}$)	P$^+$(mils)
Inhibitor S2	Cl^-	1100	10	3.3	7.0
		3003	5	1.6	3.4
	Cu^{+2}	1100	0	0	0
		3003	5	1.6	3.4
	Fe^{+3}	1100	25	8.2	17
		3003	30	9.9	21
	$Cl^- + Cu^{+2} + Fe^{+3}$	1100	70	23	49
		3003	55	18	38
50% E.G. + 0.05% Inhibitor C	Cl^-	1100	220	73	150
		3003	180	59	120
	Cu^{+2}	1100	160	57	120
		3003	260	79	170
	Fe^{+3}	1100	65	21	44
		3003	25	8	17
	$Cu^{+2} + Fe^{+3} + Cl^-$	1100	340	112	240
		3003	330	108	230

[+] Maximum probable pit penetration depth on a lifesize plant (1.5 x 10^5 cm^2) in 20 years.

[*] At 200 ppm each.

TABLE XI

HIGH TEMPERATURE PERFORMANCE TEST OF INHIBITED GLYCOL SOLUTIONS WITH CONTAMINANTS*

(at 160°C)

Base Solution	pH Before	pH After	Time (days)	ΔW(mg)	R_{corr}(mpy)
Inhibitor A1	9.9	8.1	11	23.5	4.4
Inhibitor Formula II	11.2	7.0	11	18.5	3.4
Inhibitor S1	7.4	6.6	7	16.0	4.7
E.G. + 0.1% Inhibitor C	5.0	4.0	10	39.2	8.0
E.G. + 1% Inhibitor C	7.6	2.0	11	44.1	8.2

---

*$CuSO_4$, NaCl and $Fe_2(SO_4)_3$ at 200 ppm each

C. Task III - Further Development of Techniques to Assess Corrosion Damage

Thin foil method was used to verify the results reported in Section III.B. Inhibitors A1, S1 and S2 were examined with aluminum foil samples (1100 series aluminum). A weight loss method was used to determine the corrosion rates. The results are shown in Table XII. They appear to be in good agreement with the corrosion rates obtained using the linear polarization resistance method. It was noted that the samples exposed to Inhibitor S2 solution (with Cu, Fe and NaCl at 200 ppm each) were perforated by pitting attack. Similar effect was observed and reported in Section III.B.3.b. Inhibitors A1 and S1 seem to have effectively protected the foil samples from pitting. These results fully demonstrated the fact that the thin foil method is indeed effective and can be practically applied to measure the extent of corrosion.

D. Task V - Development and Study of the Effects of Chemical Scavengers for Contaminants

Some preliminary investigations were performed during the reporting period regarding this task. Since copper ions are responsible for severe deposition types of localized pitting attack on aluminum, an experiment was performed to determine the effect of copper ion concentration on the pitting corrosion of aluminum. The ultimate objective is to determine the threshold concentration for such pitting attack to occur if it exists. Aluminum sheet samples were exposed to 50 vol % ethylene glycol solutions with $CuSO_4$ added at 200, 20, 2 and 0.2 ppm for 2 weeks at 100°C to induce pits. The results are reported in Table XIII. Although the pit density was seen to decrease with lower copper ion concentration, maximum pit depth was not found to be affected appreciably by this change. $CuSO_4$ at 0.2 ppm in solution still poses serious threat to aluminum. Aluminum samples were also immersed in a 50 vol % ethylene glycol solution with 0.2 ppm $CuSO_4$ and 200 ppm Na_2SO_4 (the latter was added just to increase the electrical conductivity). It was found that pitting propagation is more rapid in this solution. Any chemical scavenger developed in this task will thus have to be able to reduce the copper

TABLE XII

ALUMINUM CORROSION IN INHIBITED GLYCOL SOLUTIONS
USING THIN FOIL SAMPLES

(At T = 110^{o}C, Period = 15 days, sample area = 3 in^{2})

Solution	Additive(s)*	Δm(mg)	R_{corr}(mpy)	Remarks
50% Inhibitor A1	none	0.7	0.12	
	Cl^{-}	0.7	0.12	
	Cu^{+2}	2.2	0.40	
	Fe^{+3}	0.7	0.12	
	$Cu^{+2}+Fe^{+3}+Cl^{-}$	3.8	0.70	
Inhibitor S1	None	5.4	1.0	
	$Cu^{+2}+Fe^{+3}+Cl^{-}$	5.4	1.0	
Inhibitor S2	None	6.2	1.1	Pitted
	$Cu^{+2}+Fe^{+3}+Cl^{-}$	6.3	1.2	Pitted

---

*at 200 ppm each

TABLE XIII

EFFECT OF COPPER ION CONCENTRATION ON THE PITTING CORROSION OF ALUMINUM ALLOYS IN 50 Vol% ETHYLENE GLYCOL SOLUTIONS

(T = 100°C, 2 weeks, Sample area 102.3 cm^2)

Cu^+ (ppm)	Alloy	D(μ)	K(μ/day$^{1/3}$)	P^+(mils)
200	1100	125	52	110
	3003	120	50	106
20	1100	110	46	97
	3003	110	46	97
2	1100	100	41	87
	3003	90	37	78
.2	1100	95	39	83
	3003	60	25	53
.2 + 200 ppm Na_2SO_4	1100	210	87	180
	3003	160	66	140

[+] Probable penetration depth on a life size plant with $1.5x10^5$ cm^2 exposed surface area in 20 years.

ion concentration to below 0.2 ppm unless proper corrosion inhibitors are also incorporated in the corrosion control methods.

IV. REFERENCES

1. M. Stern and A. L. Geary, J. Electrochem. Soc., 104, 56 (1957).
2. S. Evans and E. L. Koehler, J. Electrochem. Soc., 108, 509 (1961).
3. M. S. Walker and W. D. Frances, Jr., Materials Protection, 8, 47 (1969).
4. M. S. Walker, Materials Performance, July, 37 (1974).
5. C. Wagner and W. Traud, Z. Electrochem., 44, 391 (1938).
6. F. Mansfeld and K. B. Oldham, Corrosion Science, 11, 787 (1971).
7. H. P. Godard, W. D. Jepson, M. R. Bothwell and R. L. Kane, *Corrosion of Light Metals*, p. 60, John Wiley and Sons, Inc. (1967).
8. H. H. Uhlig, *Corrosion Handbook*, p. 1052, Wiley, New York (1948).
9. S. C. Byrne, Solar Age, 19, May (1977).
10. M. S. Walker, Materials Performance, 12, 29 July (1973).
11. General Motors Engineering Standards, GM 6038-M.

☆U.S. GOVERNMENT PRINTING OFFICE: 1978-740-300 4308REGION NO. 4