345
11-12-80
JMB

10. 1992
DOE/CS/31072-T2

STUDY OF ALUMINUM CORROSION IN ALUMINUM SOLAR HEAT
COLLECTORS USING AQUEOUS GLYCOL SOLUTION FOR HEAT
TRANSFER

MASTER

Annual Technical Progress Report, July 30, 1979—July 31, 1980

By
David Wong
Franklin H. Cocks

August 1980

Work Performed Under Contract No. AC04-79CS31072

Giner, Inc.
Waltham, Massachusetts

U.S. Department of Energy

Solar Energy

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

"This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

This report has been reproduced directly from the best available copy.

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

Price: Paper Copy \$6.00
Microfiche \$3.50

STUDY OF ALUMINUM CORROSION IN ALUMINUM SOLAR HEAT
COLLECTORS USING AQUEOUS GLYCOL SOLUTION FOR HEAT TRANSFER

Annual Technical Progress Report
July 30, 1979 - July 31, 1980

By:

David Wong
and
Franklin H. Cocks

GINER, INC.
14 Spring Street
Waltham, MA 02154

Prepared for:

Office of Solar Applications
U. S. DEPARTMENT OF ENERGY

Under Contract No. DE-AC04-79CS31072

AUGUST 1980

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

	<u>Page No.</u>
ABSTRACT	iii
I. INTRODUCTION	1
A. Background	
B. Summary of Previous Work	
C. Scope of Present Contract	5
II. EXPERIMENTAL METHODS	6
A. Preparation of Inhibited Ethylene and Propylene Glycols	
B. Aging of Glycols at Elevated Temperatures	
C. Laboratory Corrosion Tests	8
D. Measurement of Critical Pitting Potential of Aluminum in Aqueous Ethylene Glycol Solutions	
III. RESULTS AND DISCUSSION	10
A. Aging of Glycol at Elevated Temperatures	
B. Corrosiveness of Aged Glycols to Aluminum	11
C. Critical Pitting Potential Measurements	12
IV. FIGURES AND TABLES	
Figures 1 - 15	
Tables I - V	
V. CONCLUSIONS	36
VI. REFERENCES	37

ABSTRACT

Aluminum solar heat collectors operating on aqueous glycol heat transfer fluids are potentially attractive except for the critical problem of pitting corrosion. The ultimate goal of this program is to develop means whereby light gage aluminum solar collector panels and aqueous glycol solutions can be used safely over extended periods of time.

In our previous work the extent of this aluminum corrosion problem has been determined quantitatively. Several corrosion control techniques were also developed and evaluated based on short-term laboratory corrosion tests. It was concluded that the combined use of conventional inhibitors and suspended zinc powder is extremely effective in totally stopping aluminum corrosion, including pitting. Zinc powder in suspension plays the dual role both as a heavy metal ion getter and a floating sacrificial anode. In the latter case, the aluminum is polarized through electrical contact with zinc powder to below its critical pitting potential even in a chloride-ion containing medium.

This present work is addressed both to the study of the effects of glycol aging at elevated temperatures over long periods of time and to the optimization of the zinc powder protective technique. Glycols are known to gradually decompose into organic acids at high temperatures. These product species may be aggressive to aluminum in the long run. In addition, corrosion inhibitors may also breakdown due to continuous exposure to high temperatures. As for the zinc powder protective technique, efforts have been made to determine the optimal conditions under which aluminum solar collector panels can be protected most effectively and economically.

Both uninhibited and inhibited ethylene as well as propylene glycols have been aged at three different temperatures (100, 140, and 190°C) for 6000 hours continuously. Aliquot samples were taken at 1000 hour intervals for pH measurement and chemical analysis. Results showed that in most cases solution pH dropped sharply during the first 1000 hours of exposure and gradually decreased at a slower pace as the aging process progressed. It was also noted that higher temperatures appeared to hasten this pH shift. The corrosiveness of these aged glycol solutions towards aluminum was determined based on laboratory corrosion tests. It was found that the glycols became more corrosive with increasing aging temperature. For example, one inhibited glycol became extremely corrosive to aluminum after 3000 hours at 180°C while the same solution was found to still render satisfactory corrosion protection to aluminum after 5000 hours of exposure at 100°C.

The critical pitting potential (E_p) of aluminum in chloride-ion containing aqueous glycol solutions was determined. Its dependence on temperature, chloride-ion concentration, and glycol content was investigated in detail. Such information is essential in the protection of aluminum using the zinc powder protective method because aluminum is immune from pitting only when it is polarized to below this pitting potential. E_p was found to become more negative with higher chloride-ion concentration, increasing temperature, and decreasing glycol content.

I. INTRODUCTION

A. Background

Solar thermal energy collector systems using light gauge, roll-bonded aluminum panels, together with aqueous glycol solutions for heat transfer are potentially very attractive based on both economical and technological considerations. The advantages include low cost, low density, high thermal conductivity and ease of fabrication of aluminum alloys, as well as low cost, ready availability, reasonable heat capacity and combined antifreezing/antiboiling properties of aqueous glycol solutions. However, such a combination is presently hampered by the critical problem of aluminum corrosion which would lead to catastrophic early plant failure.

Aluminum and its alloys are electrochemically active and capable of evolving hydrogen in an aqueous environment. However, aluminum is still considered to be corrosion resistant for as long as its protective oxide layer remains undisturbed. Once this oxide film is disrupted and its healing prevented, aluminum is then susceptible to various kinds of corrosion in aqueous media. Localized pitting corrosion is of particular concern since most of the corrosion perforations found in light gauge aluminum structures can be attributed to pitting corrosion. The goal of this program is then to develop and ascertain means whereby aluminum solar heat panels and water/glycol heat transfer fluids can be safely used over extended periods of time without suffering significant corrosion damage.

B. Summary of Previous Work

The study of corrosion and its control in aluminum solar heat collector systems was originally performed under Contract EY-76-C-02-2934 with ERDA (later DOE) during the period June 1, 1976 - July 31, 1978. The first phase (June 1, 1976 - May 31, 1977) was addressed to the acquisition of baseline

aluminum corrosion data in order to determine the extent of corrosion problems to be dealt with in actual solar heat collector systems⁽¹⁾. In Phase II (June 1, 1977 - July 31, 1978), the emphasis was then shifted to the development of corrosion control methods (primarily inhibitors) and the evaluation of such methods based on short term laboratory tests⁽²⁾.

1. Summary of Phase I

Corrosion characteristics of selected aluminum compositions in a 35 vol % aqueous ethylene glycol solution were obtained under conditions relevant to the operation of actual solar heat collector systems. The linear polarization resistance technique was used to determine the overall corrosion rate. Maximum pit depth was measured using a quantitative metallographic method. In addition, the susceptibility of tested aluminum alloys to stress corrosion cracking (SCC) and the extent of damage due to galvanic corrosion (when aluminum is in electrical contact with copper) were also investigated. The range of conditions studied included the following:

- (a) four aluminum compositions: 99.9% Al, 1100, 3003 and 3004 alloys;
- (b) 25 - 100°C;
- (c) stagnant solutions, laminar and turbulent flows;
- (d) effect of dissolved oxygen; and
- (e) effects of common contaminants (Cl^- , Cu^{+2} and Fe^{+3}).

The significant findings are:

(a) All four aluminum compositions tested show marginally acceptable corrosion resistance (including pitting corrosion) in pure aqueous ethylene glycol solutions.

(b) The presence of either Cl^- or Cu^{+2} (or a combination of both) can induce severe pitting attack on aluminum. Ferric (Fe^{+3}) ions are responsible for a very rapid and more or less uniform type of corrosion damage. The presence

of either one of the three species will definitely lead to catastrophic plant failure.

(c) Neither dissolved oxygen nor hydrodynamic conditions (range 0-100 cm/sec) was found to significantly affect the measured aluminum corrosion rates.

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

(e) Galvanic corrosion appears to be negligible when aluminum (in contact with copper) is exposed to pure aqueous ethylene glycol solutions (electrical conductivity = 3.0×10^{-6} mho/cm) up to 100°C. However, as the solution conductivity increases, severe deposition type of corrosion has been observed. The extent of corrosion, of course, depends on the anode (aluminum) to cathode (copper) area ratio as well as the resistivity of the electrolyte.

2. Summary of Phase II

After the corrosion problems were identified and the rates quantitatively defined in Phase I, we then shifted our efforts to the development and evaluation of corrosion control methods with special considerations towards pitting corrosion. Corrosion inhibitor formulations capable of stopping aluminum corrosion and compatible with the water-glycol medium were first selected from available literature and then tested using techniques developed in Phase I. Several proprietary corrosion inhibitor formulas developed specifically for solar heat collector applications were also evaluated in this phase of the program. In addition to conventional corrosion inhibitors, active metals (e.g. Zn and Al) were added to the aqueous glycol solution as heavy metal ion scavengers to reduce its corrosiveness to aluminum. Finally, similar work was extended to the aluminum-propylene glycol combination because of the low toxicity of aqueous propylene glycol solutions.

The significant accomplishments and major findings are:

(a) Among all the inhibitor formulas tested, the ones commonly found in commercial automotive coolants appeared to be most effective in stopping aluminum corrosion (including pitting) at temperatures below 100°C even with the simultaneous presence of both chloride and heavy metal ions.

(b) A preferred inhibitor formulation for ethylene glycol is (in g/liter): $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (4.5), NaNO_3 (2.0), $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (10.0), $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (1.5), NaMBT 50% solution (5.5), and NaOH (2.0); and a preferred inhibited propylene glycol contains (in g/liter): $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (4.0), NaNO_3 (2.0), $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (1.0), $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (6.0), NaMBT 50% solution (5.5) and NaOH (1.0).

(c) At temperatures above 130°C, the inhibitor formulations stated in (b) above become less effective. Reappearance of pitting corrosion under these conditions was observed.

(d) Propylene glycol is, in general, less corrosive to aluminum than ethylene glycol.

(e) Zinc metal was found to be not only effective as a scavenger of Cu^{+2} and Fe^{+3} but also as floating sacrificial anodes (when used as powder in suspension) which cathodically protected aluminum from pitting corrosion in chloride ion containing media. The contact between zinc powder and aluminum successfully lowered the potential of aluminum to below its critical potential.

(f) The combined use of zinc powder and corrosion inhibitors was found to be capable of stopping aluminum corrosion (including pitting) at temperatures up to 160°C based on short term laboratory tests.

C. Scope of Present Contract (July 30, 1979 - Jan. 31, 1981)

Since most of the above conclusions were based on relatively short term experiments, the emphasis for the present contract is placed on the study of the effects of aging taking place at elevated temperatures (above 100°C) on both ethylene and propylene glycol based solutions. Glycols are known to be susceptible to thermal decomposition with the concomitant formation of organic acids. Inhibitors may break down due to long term exposure to elevated temperatures. These changes of glycol solution characteristics and the consequent effects on the corrosiveness of these solutions to aluminum are being determined quantitatively during the present contract.

Another research area (not included in the original statement of work but added to the present contract through a recent contract modification) is the optimization of the use of zinc powder to control aluminum corrosion. This includes a study of the critical pitting potential of aluminum in chloride-ion containing aqueous glycol solutions, an investigation of the corrosion behavior at zinc and Zn - Al alloys in aqueous glycol solutions particularly in the potential region where aluminum is free from pitting (slightly more cathodic than the critical pitting potential), and finally the effects of particle size and morphology of zinc (or Zn - Al) powder on the cathodic protection of aluminum from chloride-ion initiated pitting corrosion.

Upon completion of the program, a corrosion control manual will be prepared and made available to solar heat collector system builders and operators. This manual will include procedures and methods developed for minimizing corrosion damage in aluminum solar heat collectors including quantitative formulas for inhibiting agents; type and concentration of glycol to be used and a description of the principles and design of several implantable corrosion monitoring devices.

II. EXPERIMENTAL METHODS

A. Preparation of Inhibited Ethylene and Propylene Glycols

Inhibited ethylene glycol solution was prepared according to the formulation developed and tested in our previous work. The composition (in g/liter) is: $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (4.5), NaNO_3 (2.0), $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (10.0), $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (1.5), NaMBT 50% solution (5.5), and NaOH (2.0). All chemicals used are Baker reagent grade. Special mixing procedures are followed in order to minimize the formation of insoluble species. Sodium Borate is added directly to ethylene glycol under mild heating and agitation. The remaining inhibitory agents, except NaMBT solution, are separately dissolved in small amounts of warm distilled water (less than 2 wt % total) and then poured into the premixed ethylene glycol/sodium borate solution. Finally, sodium MBT is added to this mixture to complete this preparation work.

As for inhibited propylene glycol solution, a slightly different formula consisting of the following inhibitory agents (in g/liter): $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (4.0), NaNO_3 (2.0), $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (1.0), $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (6.0), NaMBT 50% solution (5.5) and NaOH (1.0) is used in this program. This variation is solely based on solubility considerations. Similar mixing procedures to those described above are taken to minimize the formation of any insoluble species.

B. Aging of Glycols at Elevated Temperatures

Three identically prepared inhibited ethylene glycol solutions (without aluminum) are aged at 100, 140 and 190°C, respectively. Three identical samples of Baker reagent grade ethylene glycol are also subjected to the same aging conditions in order to obtain a measure of the effect of pure glycol thermal decomposition for comparison. In addition, 200 ppm each of NaCl, CuSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ are added to three additional inhibited ethylene glycol solutions to simulate the presence of common contaminants in actual solar collector systems. These contaminated and inhibited ethylene glycol solutions are also aged at these

three selected temperatures in order to determine the roles of these deleterious species (with respect to aluminum corrosion) in the degradation of both ethylene glycol as well as the inhibitors as functions of time and temperature. Solutions aged at both 100 and 140°C are contained in Pyrex vessels immersed in two separate constant temperature baths. High temperature limiting thermostats are installed in addition to the thermoregulators attached to the heater/circulator units to protect the baths from accidental overheating. As for the aging processes taking place at 190°C a refluxing method is used. Each solution is placed in a round bottom flask with a water-cooled condenser attached to avoid rapid loss of glycol due to evaporation. The flask is heated by a heating mantle, and the temperature is regulated ($\pm 1^\circ\text{C}$) by a Fenwal Model 543 Controller with a thermocouple input. All solution temperatures are monitored on a daily basis.

Similar arrangements were made to age propylene glycol solutions. The temperatures chosen for the aging of propylene glycol are 100, 140 and 180°C, respectively. The selection of 180°C (instead of 190°C) was based on propylene glycol boiling point consideration.

An aliquot sample (at ~ 100 ml each) of each solution is taken from each vessel after every 1000 hours of exposure to elevated temperatures. A small quantity (~10 ml) of each aged glycol sample was used to prepare first an 85 vol % aqueous glycol solution by mixing it with an appropriate amount of distilled water. The pH of this solution is then measured at ambient temperature using an Orion Model 801A pH meter. This 85 vol % aqueous aged glycol solution is further diluted to 50 vol % solution by adding more distilled water to it for a second pH measurement.

A gas chromatographic analysis is performed for each aged glycol sample to determine any chemical composition changes.

C. Laboratory Corrosion Tests

The corrosiveness of each aged glycol solution towards aluminum is quantitatively determined using the following laboratory corrosion test: A set of aluminum corrosion samples consisting of one 1100 series sheet approximately 2" x 2" x 1/16" in size and one 1100 series 1 mil foil with exposed area approximately 1 1/2" x 1" is immersed in each aged glycol solution (50 vol % aqueous) for 7 days. The temperatures chosen are 100 and 130°C. The aluminum sheets are polished with 320 and 600 grit SiC paper and then annealed before use. Weight loss measurements are made for both foil and sheet samples. These samples are also examined metallographically for possible signs of pitting.

The foil sample offers a large surface area to mass ratio and an increased sensitivity of this gravimetric method. In addition, pitting perforation through a 1 mil thickness usually occurs in a relatively short period of time and the pitting can then be visually detected easily.

D. Measurement of Critical Pitting Potential of Aluminum in Aqueous Ethylene Glycol Solutions

The critical pitting potential of 1100 series aluminum is determined in deaerated aqueous ethylene (and propylene) glycol solutions containing various amounts of NaCl using a step-by-step potentiostatic technique⁽³⁾. A chloride ion concentration range from 10^{-4} to 1M and four temperatures (25, 50, 70 and 100°C) are covered by this work. The procedure is to immerse the electrode (aluminum) in the chloride ion containing ethylene glycol solution for a few minutes while monitoring its open circuit potential versus a reference electrode (e.g. SCE or Ag-AgCl) to ensure a steady state condition has been reached. This electrode is then polarized anodically (in the positive direction) using a Wenking Model 121 potentiostat using a step-by-step method to drive the electrode potential by a 5 mV step every 5 minutes. The corresponding current is carefully

recorded. The current remained relatively constant below a certain potential but increased sharply above this potential by two to three orders of magnitude (indicative of the onset of pits). The most positive potential (E_p) at which the corresponding anodic current density stayed below $1 \mu\text{A}/\text{cm}^2$ for over 12 hours is defined as the critical pitting potential. The reproducibility is ± 5 mV.

The aluminum samples used are mounted in a glass filled diallyl phthalate molding compound with an annulus of aluminum exposed at one end. The sample is drilled and tapped from behind to make electrical contact. The exposed surface area is $\sim 1.18 \text{ cm}^2$. All samples are annealed at 345°C and then polished with 320 and 600 grit SiC paper.

A jacketed all-glass electrochemical cell with temperature regulating precision up to $\pm 0.5^\circ\text{C}$ (by a Haake constant temperature bath) is used. Pre-purified and presaturated nitrogen is used to deaerate the solution. A piece of chloridized silver wire (Ag-AgCl electrode) is used as the reference electrode. Its potential versus a saturated calomel electrode is determined after each critical pitting potential measurement in order to convert all the potentials to standard hydrogen electrode potential based on available thermodynamic data from open literature (4-6). An Ag-AgCl electrode is chosen over a SCE because of the possible contamination of the solution with Cl^- ions by the SCE, which will significantly increase the chloride ion concentration (perhaps by 1-2 orders of magnitude) for aqueous glycol solutions containing less than 10^{-3}M NaCl. Two graphite rods are used as counter electrodes for uniform current distribution.

III. RESULTS AND DISCUSSION

A. Aging of Glycol at Elevated Temperatures

All glycol aging experiments were completed by the end of this reporting period. Both uninhibited and inhibited ethylene glycols (as well as propylene glycol) were aged at three different temperatures for up to 6000 hours continuously. Aliquot samples of these aged glycols were taken at 1000 hour intervals for pH measurement, gas chromatographic analysis, and aluminum corrosion test.

1. pH Measurement

Both 50 and 85 vol % aqueous solutions of each aged glycol sample were prepared and their pH values determined with the results shown in Table I. In general, all glycols were found to become more acidic with increasing exposure time. These results are also presented as pH versus time plots in Figures 1 - 6 for further analysis. It was first noted that ethylene glycol and propylene glycol based solutions behaved very similarly at a given aging temperature. When aged at 100°C, solution pH of glycol was found first to drop by ~2 pH units during the first 1000 - 2000 hours of exposure and then continue decreasing at a much slower rate. The presence of added impurities such as NaCl, CuSO₄, Fe₂(SO₄)₃ did not appear to affect the pH shift significantly (see Figures 1 and 2). The initial pH drop was found to be sharper and the impurities seemed to accelerate this pH shift when glycols were aged at 140°C. (see Figures 3 and 4). The presence of these impurities appeared to accelerate the pH drop somewhat. We also noted a second sharp pH drop occurring during the 5000 - 6000 hour period for ethylene glycol based solutions. This second drop may indicate the presence of a new series of glycol decomposition products at that stage. As the aging temperature further increases to 190°C and 180°C for ethylene glycol and propylene glycol based solutions, respectively, the rate of pH drop of glycol solution becomes even larger. Uninhibited glycols aged for 5000 hours were found to be at ~pH 3, which is very corrosive for

aluminum. Even inhibited glycol solutions with initial pH value at ~11 was found at pH 5 after 6000 hours of exposure to this high temperature. (see Figures 5 and 6). It was also discovered here that the presence of impurities is causing an accelerated pH change at this temperature.

2. Gas Chromatographic Analysis

Both fresh and aged glycol samples were injected into a Varian series 2700 aerograph to obtain quantitative glycol decomposition data. Unfortunately, the present column failed to separate glycol from its decomposition products. A new gas chromatographic column is being prepared for this application. When this new column is installed, experiments will resume in order to determine the fraction of glycol remained as a function of aging time.

B. Corrosiveness of Aged Glycols to Aluminum

1100 series aluminum samples both in sheet and foil forms were exposed to all the aqueous aged glycol solution (102 in total) for 7 days at 100°C. Weight loss measurements were performed and reasonably good agreement was reached between results obtained using foil and sheet samples. The results expressed in mils of penetration depth per year (mpy) are shown in Table II.

In an attempt to further coordinate these results, they are also shown graphed in Figures 7-12. Figures 7 and 8 show the aluminum corrosion rate versus aging time in ethylene and propylene glycol solutions aged at 100°C, respectively. At this aging temperature (100°C), aluminum corrosion rates were found to be below 1 mpy even up to 5000 hours of exposure regardless whether inhibitors were present. Pits were observed only on one sample immersed in uninhibited ethylene glycol solutions. However, corrosion rates were found to increase to above 1 mpy (which is considered to be the safety margin for light gauge aluminum solar collectors) when solutions were exposed for 6000 hours especially in uninhibited glycol solutions. Based on the above, it is concluded that inhibited glycol solutions may be considered to be safe for up to 5000 operating hours at temperatures below 100°C.

When aged at 140°C , aluminum corrosion rate in uninhibited glycol solutions was found to exceed the 1 mpy limit after 4000 hours. Pitting corrosion was observed in many cases. Corrosion inhibitors only provided marginal protection after 4000 - 5000 hours of exposure to this temperature (see Figures 9 and 10). As the aging temperature increased further to 180 or 190°C , uninhibited ethylene glycol becomes extremely corrosive to aluminum in less than 1000 hours (see Figures 11 and 12). Inhibitors were found to lose their strength in about 3000 hours. Pitting corrosion was found to be very serious. Many foil samples were perforated in the one week testing period.

It is important to emphasize that these corrosion rates were obtained at 100°C . This result thus indicates that once the glycol solutions are exposed to elevated temperatures they become extremely corrosive to aluminum even at a lower temperature. In other words, glycol heat transfer fluids subjected to stagnation conditions may undergo irreversible changes which can be detrimental to the collector panels.

4. Visual Observation

Among all the glycols aged in this program, only pure ethylene and propylene glycols aged at 100°C did not change color in 6000 hours. The remaining 15 solutions became much darker in color upon completion of the aging experiment. Especially, those inhibited glycol solutions almost became completely opaque (black), indicative of chemical composition changes during the aging process. In many cases, precipitates were found in these inhibited glycols which might hinder the heat transfer property of the aluminum solar collector panel.

C. Critical Pitting Potential Measurements

The critical pitting potential (E_p) of 1100 series aluminum in deaerated aqueous ethylene glycol solutions has been determined as functions of both temperature and sodium chloride concentration. These results are shown in Table III. These critical pitting potentials, which are reported in millivolts

with respect to the standard hydrogen electrode (SHE), are essentially information needed in the cathodic protection of aluminum (i.e. zinc powder protective technique) from pitting in aqueous ethylene glycol media.

It was found that the critical pitting potential of aluminum is a strong function of chloride concentration. Specifically, E_p becomes more negative as the chloride concentration increases. Furthermore, contrary to what Uhlig, et al.⁽³⁾ found, we observed that E_p does depend on temperature within the range between 25 to 100°C. For the same chloride concentration, E_p is more negative as the temperature rises. Since protection of aluminum from pitting using zinc powder is achieved by lowering its potential to below E_p , it becomes more difficult to achieve complete protection as E_p gets more negative. This result implies that more zinc powder must be used to accomplish total protection.

When plotting E_p versus $\log (Cl^-)$, we found linear behavior at all four temperatures (see Figure 13). The following empirical expressions are obtained:

$$E_p \text{ (mV vs. SHE)} = -529 - 62.2 \log (Cl^-) \text{ at } 25^\circ\text{C} \quad (1)$$

$$E_p \text{ (mV vs. SHE)} = -586 - 64.5 \log (Cl^-) \text{ at } 50^\circ\text{C} \quad (2)$$

$$E_p \text{ (mV vs. SHE)} = -630 - 74.0 \log (Cl^-) \text{ at } 70^\circ\text{C} \quad (3)$$

$$\text{and } E_p \text{ (mV vs. SHE)} = -668 - 75.0 \log (Cl^-) \text{ at } 100^\circ\text{C} \quad (4)$$

Similar results were reported by other researchers^(3,7) for aluminum in pure aqueous NaCl solutions at 25°C, as follows:

$$E_p \text{ (mV vs. SHE)} = -504 - 124 \log (Cl^-) \quad (5)$$

Comparing (5) to (1), one is able to conclude that in the presence of ethylene glycol, the dependence of E_p on $\log (Cl^-)$ ($dE_p/d \log (Cl^-)$) is about $\frac{1}{2}$ of that in pure aqueous solutions.

The critical pitting potential of 1100 series aluminum was also measured as a function of ethylene glycol concentration in chloride-ion containing media. The results are tabulated in Table IV. It was found that E_p becomes more positive almost linearly with increasing ethylene glycol content in a region ranging from

35 - 85 vol % at all temperatures. The sharp rise of E_p in the positive direction in the almost non-aqueous (99.97%) media shown in Figure 14 is most probably attracted by the junction potential between SCE and ethylene glycol which was not taken into consideration in these experiments.

It was also noted from this set of data that the critical pitting potential of aluminum at 70°C depends on the history of the sample. E_p obtained using a sample warmed up to 70°C from 25°C was found to be more negative than the one measured with the same sample cooled down from 100°C. The difference can be as much as 100mV. At 25 and 100°C, however, sample history was found to be totally irrelevant. This effect is most probably attributed to the phase transformation from that low temperature of aluminum oxide ($Al_2O_3 \cdot 3H_2O$) into a high temperature oxide ($Al_2O_3 \cdot H_2O$) in the 70°C region. Since bohmite ($Al_2O_3 \cdot H_2O$) is believed to be more protective, the potential at which it begins to breakdown is then, of course, expected to be higher (more positive) than the one at which the lower temperature oxide ($Al_2O_3 \cdot 3H_2O$) starts to fail.

The critical pitting potential of 1100 series aluminum in a 50% aqueous propylene glycol solution was obtained. The results are shown in Table V. Plots of E_p vs. $\log (NaCl)$ also yield straight lines (see Figure 15). The following empirical expressions are found:

$$E_p \text{ (mV vs. SHE)} = -539 - 59.0 (Cl^-) \text{ at } 25^\circ C \quad (6)$$

$$E_p \text{ (mV vs. SHE)} = -692 - 71.0 (Cl^-) \text{ at } 70^\circ C \quad (7)$$

These are very similar to equations (1) and (3) obtained in aqueous ethylene glycol solutions.

IV. FIGURES AND TABLES

Figures 1 - 15

Tables I - V

Figure 1. Ethylene Glycol Based Solutions Aged at 100°C

Figure 2. Propylene Glycol Based Solutions Aged at 100°C

Figure 3. Ethylene Glycol Based Solutions Aged at 140°C

Figure 4. Propylene Glycol Based Solutions Aged at 140°C

Figure 5. Ethylene Glycol Based Solutions Aged at 190°C

Figure 6. Propylene Glycol Based Solutions Aged at 180°C

Figure 7. Aluminum Corrosion in Ethylene Glycol Solutions Aged at 100°C

Figure 8. Aluminum Corrosion in Propylene Glycol Solutions Aged at 100°C

Figure 9. Aluminum Corrosion in Ethylene Glycol Solutions Aged at 140°C

Figure 10. Aluminum Corrosion in Propylene Glycol Solutions Aged at 140°C

Figure 11. Aluminum Corrosion in Ethylene Glycol Solutions Aged at 190°C

Figure 12. Aluminum Corrosion in Propylene Glycol Solutions Aged at 180°C

Figure 13. Critical Pitting Potential of Aluminum in 50 vol% Ethylene glycol

Figure 14. Critical Pitting Potential of Aluminum in Aqueous Ethylene Glycol Solutions Containing 6.3×10^{-3} M NaCl (approximately 360 ppm)

Figure 15. Critical Pitting Potential of Aluminum in Aqueous Propylene Glycol Solutions

TABLE I
pH OF AGED AQUEOUS GLYCOL SOLUTIONS

Solution	Inhibitors	Contaminants*	Fresh	pH									Aged 3000 hrs at:			Aged 4000 hrs at:			Aged 5000 hrs at:			Aged 6000 hrs at:		
				Aged 1000 hrs at:			Aged 2000 hrs at:			Aged 3000 hrs at:			Aged 4000 hrs at:			Aged 5000 hrs at:			Aged 6000 hrs at:			Aged 6000 hrs at:		
				100°C	140°C	190°C	100°C	140°C	190°C	100°C	140°C	190°C	100°C	140°C	190°C	100°C	140°C	190°C	100°C	140°C	190°C	100°C	140°C	190°C
ETHYLENE GLYCOL																								
85 vol %	No	No	6.53	4.75	5.80	4.28	5.11	5.60	3.87	5.87	5.20	3.60	5.78	5.27	3.51	6.30	5.31	3.25	5.10	4.74	2.82			
50 vol %			6.38	4.68	5.80	4.19	5.06	5.40	3.83	5.92	5.74	3.56	5.68	4.91	3.49	6.35	4.65	3.18	5.13	4.29	2.88			
85 vol %	Yes ¹	No	11.22	10.04	11.19	10.65	8.91	10.91	8.83	8.83	10.74	8.02	8.62	10.76	7.83	8.35	10.50	7.89	8.09	7.45	8.57			
50 vol %			11.15	10.03	11.10	10.56	9.16	10.79	9.25	9.08	10.52	8.36	8.94	10.50	8.23	8.81	10.41	8.23	8.63	7.87	8.82			
85 vol %	Yes ¹	Yes	11.17	8.92	10.41	10.66	8.27	7.60	7.95	8.13	7.43	7.11	8.10	7.20	6.93	7.84	7.00	6.50	7.53	6.08	5.39			
50 vol %			11.14	9.03	10.35	10.63	8.56	8.12	8.44	8.63	7.94	7.60	8.56	7.49	7.31	8.42	7.40	6.79	8.20	5.41	5.03			
PROPYLENE GLYCOL																								
				100°C	140°C	170°C**	100°C	140°C	180°C	100°C	140°C	180°C	100°C	140°C	180°C	100°C	140°C	160°C	100°C	140°C	180°C			
85 vol %	No	No	6.02	4.39	6.40	5.30	4.12	5.46	5.70	4.68	6.60	4.70	4.56	5.94	4.70	4.62	6.47	3.95	4.82	5.72	4.03			
50 vol %			6.06	4.30	6.75	5.24	4.09	5.66	6.31	4.49	6.30	4.57	4.28	6.05	4.40	4.25	6.52	3.78	4.35	5.68	3.90			
85 vol %	Yes ²	No	11.53	10.14	8.20	9.98	8.96	7.75	10.80	9.09	7.79	7.40	8.91	7.79	6.62	8.94	7.67	6.50	9.03	7.59	5.89			
50 vol %			11.31	10.08	8.35	10.29	9.06	8.01	10.72	9.10	8.10	7.60	8.97	8.08	6.68	8.96	7.30	6.48	9.03	7.95	5.38			
85 vol %	Yes ²	Yes	11.60	-	9.98	10.54	-	8.22	10.25	-	7.77	10.19	-	7.50	10.70	-	7.08	9.71	-	7.33	10.65			
50 vol %			11.22	-	10.03	10.50	-	8.42	10.42	-	7.98	10.77	-	7.71	10.65	-	7.24	9.66	-	7.49	10.34			

¹Inhibitors in (g/liter): Na₃PO₄ · 12H₂O (4.5), NaNO₃ (2.0), Na₂B₄O₇ · 10H₂O (10.0), Na₂SiO₃ · 9H₂O (1.5), NaMBT 50% solution (5.5), and NaOH (2.0)

²Inhibitors in (g/liter): Na₃PO₄ · 12H₂O (4.0), NaNO₃ (2.0), Na₂B₄O₇ · 10H₂O (6.0), Na₂SiO₃ · 9H₂O (2.0), NaMBT 50% solution (5.5), and NaOH (1.0)

*CuSO₄, NaCl and Fe₂(SO₄)₃ at 200 ppm each.

**Initially set at 170°C and later changed to 180°C.

TABLE II
ALUMINUM CORROSION IN 50 VOL % AGED GLYCOL SOLUTIONS AT 100°C

<u>Solution</u>	<u>Aluminum Corrosion Rate (mpy) In Solution Aged For</u>																	
	<u>Aged 1000 hrs at:</u> <u>100°C</u>	<u>140°C</u>	<u>190°C</u>	<u>Aged 2000 hrs at:</u> <u>100°C</u>	<u>140°C</u>	<u>190°C</u>	<u>Aged 3000 hrs at:</u> <u>100°C</u>	<u>140°C</u>	<u>190°C</u>	<u>Aged 4000 hrs at:</u> <u>100°C</u>	<u>140°C</u>	<u>190°C</u>	<u>Aged 5000 hrs at:</u> <u>100°C</u>	<u>140°C</u>	<u>190°C</u>	<u>Aged 6000 hrs at:</u> <u>100°C</u>	<u>140°C</u>	<u>190°C</u>
Pure Ethylene Glycol	0.5	0.7	1.8	0.8	0.9	7.1	0.8	0.8	6.5*	0.3	0.9	11.7*	0.5	4.8*	11.8*	1.1	11.2*	12.5*
Inhibited Ethylene Glycol	0	0	0	0.5	0.3	0	0.3	0.5	0.5	0	0.2	0.5	0	0.2	0.5	0	1.3	1.1
Inhibited Ethylene Glycol & Impurities	0.3	0.2	0	0.5	0.1	0	0.2	0.4	0.6	0.3	0.2	0.3	0.1	1.3	1.8	1.2	-	2.7
	<u>100°C</u>	<u>140°C</u>	<u>180°C</u>	<u>100°C</u>	<u>140°C</u>	<u>180°C</u>	<u>100°C</u>	<u>140°C</u>	<u>180°C</u>	<u>100°C</u>	<u>140°C</u>	<u>180°C</u>	<u>100°C</u>	<u>140°C</u>	<u>180°C</u>	<u>100°C</u>	<u>140°C</u>	<u>180°C</u>
Pure Propylene Glycol	0.2	0.8	0.3	0.6	0.9*	0.3	0.4	0.9*	0.7	0.3	0.5	1.6	0.2	1.9*	2.0	1.1	8.0*	8.4*
Inhibited Propylene Glycol	0.2	0.4	0.5	0.2	0.1	0.2	0.2	0	0.3	0.2	0.2	1.6	0	0.2	1.4	0.2	0.7	1.5
Inhibited Propylene Glycol & Impurities	-	0	0.1	-	0	0	-	0	0	-	0.1	0.1	-	0.9	0.3	-	0.7	0.5

*Samples pitted.

TABLE III

CRITICAL PITTING POTENTIAL OF 1100 SERIES ALUMINUM
IN 50 VOL % AQUEOUS ETHYLENE GLYCOL SOLUTIONS

<u>[NaCl]</u>	<u>E_p (mV vs. SHE)</u>			
	<u>25°C</u>	<u>50°C</u>	<u>70°C</u>	<u>100°C</u>
10 ⁻⁴	-280	-330	-335	-380
10 ⁻³	-340	-380	-410	-475
10 ⁻²	-410	-475	-495	-520
10 ⁻¹	-470	-515	-560	-590
1	-530	-585	-625	-670

TABLE IV

CRITICAL PITTING POTENTIAL OF ALUMINUM IN AQUEOUS
ETHYLENE GLYCOL SOLUTIONS CONTAINING $6.3 \times 10^{-3}\text{M NaCl}$

<u>Ethylene Glycol</u> <u>Concentration (Vol %)</u>	<u>25°C</u>	<u>E_p (mV vs. SHE)</u>			<u>cool</u> <u>down</u>	<u>70°C</u>
		<u>warm</u> <u>up</u>	<u>70°C</u>	<u>—</u> <u>100°C</u>		
35	-375		-430	-480		-
50	-365		-420	-470		-320
85	-340		-370	-450		-315
99.97	-5		-20	-140		+25

TABLE V

CRITICAL PITTING POTENTIAL OF 1100 SERIES ALUMINUM
IN 50 VOL % AQUEOUS PROPYLENE GLYCOL SOLUTIONS

<u>NaCl (M)</u>	<u>E_p (mV vs. SHE)</u>	
	<u>25°C</u>	<u>70°C</u>
10 ⁻³	-355	-495
10 ⁻²	-425	-515
10 ⁻¹	-490	-640
1	-530	-690

Note: E_p at 70°C was obtained using a sample immersed in a solution heated up from 25°C.

V. CONCLUSIONS

- Solution pH values of inhibited and uninhibited ethylene (as well as propylene) glycol solutions decrease with aging time and temperature.
- Uninhibited ethylene and propylene glycol solutions become extremely corrosive to aluminum after 2000-3000 hours at 140°C and above. Solution pH drops to below 5. Most foil samples pitted through in one week.
- When aged at 100°C, aluminum seems to possess marginal corrosion resistance in these uninhibited glycol solutions for up to 5000 hours.
- Inhibited ethylene and propylene glycols aged at 100°C remained at above pH 8 for 6000 hours with or without impurities present. Aluminum corrosion tests showed that inhibitors still render satisfactory corrosion protection, in this case.
- At 140°C and above, solution pH drops sharply (to below 8) in 3000 hours. Aluminum corrosion rate increases to above 1 mpy in 3000-4000 hours, indicating the breakdown of inhibitors.
- The presence of impurities (Cu^{+2} , Fe^{+3} , NaCl) does not seem to affect the performance of inhibited glycol solutions at 100°C. However at 140°C and above, impurities accelerate both pH drop and aluminum corrosion.
- The critical pitting potential of aluminum (E_p) in aqueous glycol solutions follows a linear relationship with $\log(\text{Cl}^-)$. It becomes more negative with increasing (NaCl) and temperature.
- E_p becomes more positive with increasing glycol concentration.
- E_p obtained at 70°C depends on the history of the sample.
- The use of zinc powder is necessary to achieve complete protection against corrosion for temperatures above 100°C

VI. REFERENCES

1. J. Giner, F. H. Cocks and D. Wong, "Study of Corrosion and Its Control In Aluminum Solar Collectors," Annual Progress Report, June 1, 1976 - May 31, 1977, ERDA Report No. COO-2934-4, June (1977).
2. D. Wong, F. H. Cocks, J. Giner and P. S. Majahad, "Study of Corrosion and Its Control in Aluminum Solar Collectors," Annual Progress Report June 1, 1977 - July 31, 1978, DOE Report No. COO-2934-7, August (1978).
3. H. Bohni and H. H. Uhlig, J. Electrochem. Soc., 116, 907 (1969).
4. D. J. G. Ives and G. J. Janz, Reference Electrodes, p. 162 and 192, Academic Press, NY (1961).
5. V. V. Aleksandrov, B. N. Bezpalyi and G. Z. Dmitrenke, Elektrokimiya, 12, 144-6 (1976).
6. U. Sen, K. K. Kundu and M. N. Das, J. phys. Chem., 71, 3665-71 (1967).
7. B. N. Stirrup, N. A. Hampson and I. S. Midgley, J. Applied Electrochem. 5, 229-35 (1975).