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Semiannual Technical Progress Report, July 30, 1979—January 31, 1980

By
D. Wong
F. H. Cocks
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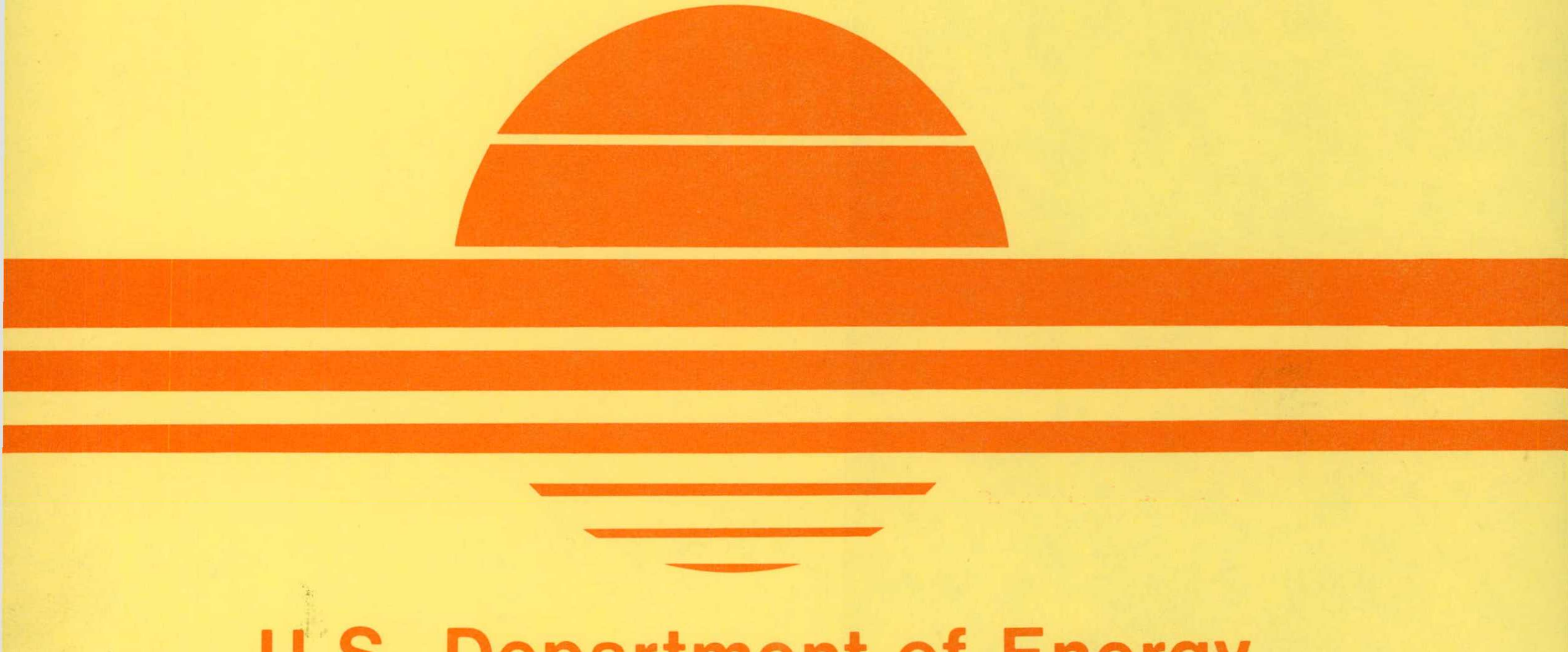
February 1980

Work Performed Under Contract No. AC04-79CS31072

Giner, Inc.
Waltham, Massachusetts



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Solar Energy

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

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

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Prepared for:
OFFICE OF SOLAR APPLICATION
U. S. DEPARTMENT OF ENERGY
Under Contract No. DE-AC04-79CS31072

February 1980

# ABSTRACT

Aluminum solar heat collector panels using aqueous glycol solutions for heat transfer appear to have many advantages. However, such a combination does suffer from significant corrosion damage primarily due to pitting corrosion of aluminum.

In our previous work the extent of this corrosion problem and several corrosion control methods were studied under conditions relevant to the operation of actual solar heat collector systems. In essence, aluminum and its alloys were found to be marginally corrosion resistant in pure aqueous glycol solutions. However, in the presence of impurities expected to exist in real systems (such as chloride, copper and iron ions), this corrosion resistance was found to decrease to an absolutely intolerable level. Corrosion inhibitors used in commercial automotive coolants were able to protect aluminum only up to temperatures of 100°C. At higher temperatures (up to 160°C), the combined use of these corrosion inhibitors and zinc powder, however, seemed to be extremely effective in totally stopping aluminum corrosion (including pitting). Zinc powder in suspension was found to render cathodic protection to aluminum even when chloride ions were present.

The present work is addressed primarily to the study of the effects of glycol aging at elevated temperatures (above 100°C). Glycols are known to be susceptible to thermal decomposition producing new product species which may be aggressive to aluminum. In addition, the possible breakdown of corrosion inhibitors due to long term exposure to high temperature will also be investigated.

Both uninhibited and inhibited ethylene (as well as propylene) glycols have been aged at temperatures up to 190°C for over 2000 hours continuously to date. Aliquot samples of each glycol solution tested in this program were taken at 1000 and 2000 hours of exposure for chemical analysis and pH measurement. Laboratory corrosion tests will be performed later to determine their corrosiveness to aluminum. Based on the data obtained so far, solution pH was found to decrease steadily with

exposure time. More samplings are expected at 3000, 4000, 5000 and 6000 hours. No other significant trend can be concluded yet.

The other aspect of this present program consists of a study of the critical pitting potential of aluminum in aqueous glycol environments. Our previous work has demonstrated that zinc powder in suspension is capable of protecting aluminum from pitting even in the presence of chloride ions by lowering its potential to below its critical potential in this type of media. The exact location of this critical pitting potential thus becomes of vital importance. Although it was not included in the original work statement, this study was added to this present program as a result of the interest generated at the project review meeting at Los Alamos in November 1979. In this report the critical pitting potential of 1100 series aluminum in a 50 vol % aqueous ethylene glycol solution is reported as functions of both temperature and chloride ion concentration. This information is essential in the cathodic protection of pitting corrosion of aluminum.

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# I. INTRODUCTION

## A. Background

Solar thermal energy collector systems using light gauge, Roll-Bond 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 leads 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. 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 solution, laminar and turbulent flows;
(d) effect of dissolved oxygen; and
(e) effects of common contaminants (e.g. $Cl^-$, $Cu^{+2}$ 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.

(d) 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 = $3.0 \times 10^{-6}$ 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): $Na_3PO_4 \cdot 12H_2O$ (4.5), $NaNO_3$ (2.0), $Na_2B_4O_7 \cdot 10H_2O$ (10.0), $Na_2SiO_3 \cdot 9H_2O$ (1.5), NaMBT 50% solution (5.5), and NaOH (2.0); and a preferred inhibited propylene glycol contains (in g/liter): $Na_3PO_4 \cdot 12H_2O$ (4.0), $NaNO_3$ (2.0), $Na_2SiO_3 \cdot 9H_2O$ (1.0), $Na_2B_4O_7 \cdot 10H_2O$ (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 - July 29, 1980)

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 need to be quantitatively determined during the present contract.

Another research area not included in the original statement of work is the study of critical pitting potential (the potential below which pitting corrosion does not occur) of aluminum in chloride ion containing aqueous glycol solutions. The concept of using zinc powder in suspension to effectively stop aluminum from pitting in the presence of chloride ions relies on the knowledge of the location of this critical pitting potential as functions of both temperature as well as chloride ion concentration. This task was added to this program due to the particular interests generated during the project review meeting at Los Alamos in November 1979.

Finally, a corrosion control manual will be prepared and made available to solar heat collector system builders and oeprators. 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: $Na_3PO_4 \cdot 12H_2O$ (4.5), $NaNO_3$ (2.0), $Na_2B_4O_7 \cdot 10H_2O$ (10.0), $Na_2SiO_3 \cdot 9H_2O$ (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): $Na_3PO_4 \cdot 12H_2O$ (4.0), $NaNO_3$ (2.0), $Na_2SiO_3 \cdot 9H_2O$ (1.0), $Na_2B_4O_7 \cdot 10H_2O$ (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 are aged at 100, 140 and 190$^\circ$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 $Fe_2(SO_4)_3$ 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. A silicone fluid is used as the heat transfer medium (instead of industrial grade ethylene glycol which has caused immersion heater failure leading to a temporary shut down during the initial period of this work) to ensure safety and continuous operation over the entire program. High temperature limiting thermoswitches 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 (instead of immersion) 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 (± 1°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 170°C, respectively. The selection of 170°C (instead of 190°C) was based on propylene glycol boiling point consideration.

Aliquot sample (at ∿ 100 ml each) of each solution is taken from each vessel after every 1000 hour period 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 a 50 vol % solution by adding more distilled water to it for a second pH measurement.

In addition to measurements of pH, a Varian series 2700 Aerograph is used for gas chromatographic analysis in order to determine any chemical composition changes as a result of the aging process.

Finally, the remaining aged glycol samples will be used in laboratory corrosion tests in order to determine their corrosiveness to aluminum and its alloys using techniques (e.g. linear polarization resistance method, weight loss measurement of corrosion coupons and foil samples, pit depth measurement, etc.) developed in our previous work.

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

The critical pitting potential of 1100 series aluminum is determined in a deaerated 50 vol % aqueous ethylene glycol solution 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 ∿ 30 minutes while its open circuit potential versus a reference electrode (e.g. SCE or Ag-AgCl) is monitored to ensure a steady state condition has been reached. This electrode is then polarized anodically 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 $\mu A/cm^2$ 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 diallylphthalate molding compound with an annulus of aluminum exposed at one end (see Figure 1). The sample is drilled and tapped from behind to make electrical contact. The exposed surface area is ∿ 1.18 $cm^2$. All samples are annealed at 345°C and then polished with 320 and 600 grit SiC paper.

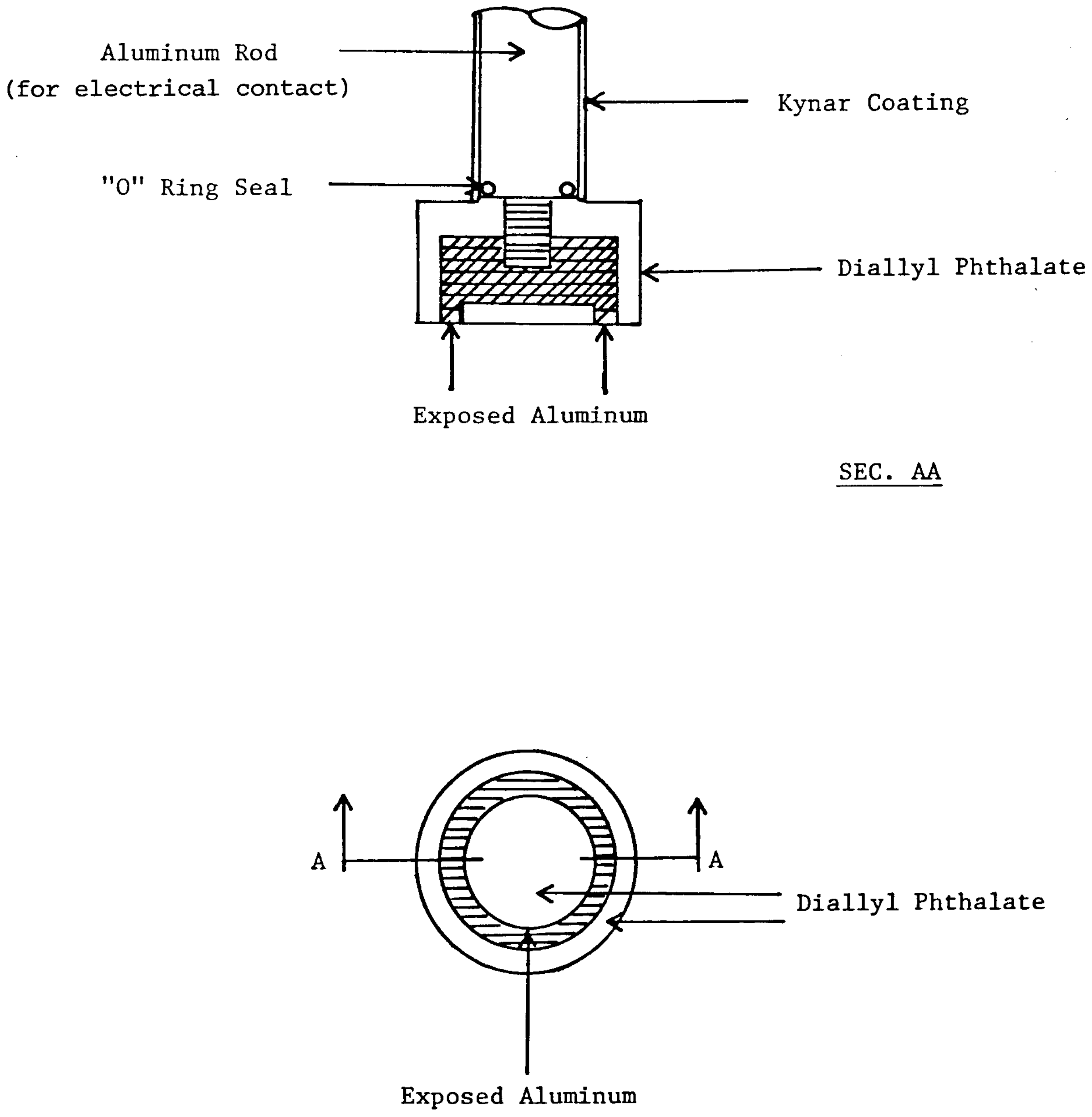

Figure 1. Configuration of Aluminum Sample.

A jacketed all-glass electrochemical cell with temperature regulating precision up to ± 0.5°C (by a Haake constant temperature bath) is used. Prepurified 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 data(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.

# III. RESULTS AND DISCUSSION

## A. Aging of Glycol at Elevated Temperatures

Both pure and inhibited ethylene, as well as propylene, solutions have been aged at three different temperatures for over 2000 hours to date. Aliquot samples of these aged glycols were taken after 1000 and 2000 hours of exposure for pH measurement, gas chromatographic analysis and laboratory corrosion test.

### 1. Measurement of pH

Aqueous solutions (50 and 85 vol %) of these aged glycol samples were prepared and their pH values determined with the results shown in Table I. In general, solution pH was found to decrease steadily (becoming more acidic) by 0.5 - 2 pH units for every 1000 hours of exposure at elevated temperatures. For ethylene glycol based solutions, solutions aged at 100 and 190°C seemed to have lower pH values as compared to identical solutions aged at 140°C. The presence of contaminants (e.g. $Cl^-$, $Cu^{+2}$ and $Fe^{+3}$) in inhibited ethylene glycol solution appeared to have caused a slight acceleration in the pH drop. As for propylene glycol based solutions, in general solution pH values first dropped for 1 - 2 pH units during the first 1000 hours of exposure and then more or less leveled off during the second 1000 hours.

In all cases the glycol solutions turned darker in color as aging progresses. All inhibited glycol solutions, despite 2000 hours of exposure to high temperatures, still maintained their pH values at $\sim$ 8 (where aluminum is known to be less susceptible to pitting)(7).

In summary, the pH values of aqueous glycol solutions are lower than those obtained from fresh solutions of identical compositions. This decrease is most probably attributed to the decomposition of glycols. However, the roles of temperature at which this process takes place and the effect of the presence of extraneous species (e.g. inhibitors, $Cl^-$, $Cu^{+2}$ and $Fe^{+3}$ etc.) are still not clear based on data available at this moment. Samples of glycol solutions aged for 3000, 4000, 5000 and possibly 6000 hours will be obtained at later dates; more conclusive evidence

# TABLE I

## MEASUREMENTS OF pH OF AGED AQUEOUS GLYCOL SOLUTIONS

| | | | | | pH | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Aged 1000 hrs at: | | | Aged 2000 hrs at: | | |
| Solution | | Inhibitors | Contaminants* | Fresh | $100^{o}C$ | $140^{o}C$ | $190^{o}C$ | $100^{o}C$ | $140^{o}C$ | $190^{o}C$ (or $170^{o}C$)** |
| Ethylene Glycol | 85 vol % | No | No | 6.53 | 4.75 | 5.80 | 4.28 | 5.11 | 5.60 | 3.87 |
| | 50 vol % | | | 6.38 | 4.68 | 5.80 | 4.19 | 5.06 | 5.40 | 3.83 |
| | 85 vol % | Yes[1] | No | 11.22 | 10.04 | 11.19 | 10.65 | 8.91 | 10.91 | 8.83 |
| | 50 vol % | | | 11.15 | 10.03 | 11.10 | 10.56 | 9.16 | 10.79 | 9.25 |
| | 85 vol % | Yes[1] | Yes | 11.17 | 8.92 | 10.41 | 10.66 | 8.27 | 7.60 | 7.95 |
| | 50 vol % | | | 11.14 | 9.03 | 10.35 | 10.63 | 8.56 | 8.12 | 8.44 |
| Propylene Glycol | 85 vol % | No | No | 6.02 | 4.39 | 6.40 | 5.30 | 4.12 | 5.46 | 5.70 |
| | 50 vol % | | | 6.06 | 4.30 | 6.75 | 5.24 | 4.09 | 5.66 | 6.31 |
| | 85 vol % | Yes[2] | No | 11.53 | 10.14 | 8.20 | 9.98 | 8.96 | 7.75 | 10.80 |
| | 50 vol % | | | 11.31 | 10.08 | 8.35 | 10.29 | 9.06 | 8.01 | 10.72 |
| | 85 vol % | Yes[2] | Yes | 11.60 | - | 9.98 | 10.54 | - | 8.22 | 10.25 |
| | 50 vol % | | | 11.22 | - | 10.03 | 10.50 | - | 8.42 | 10.42 |

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[1] Inhibitors in (g/liter): $Na_3PO_4 \cdot 12H_2O$ (4.5), $NaNO_3$ (2.0), $Na_2B_4O_7 \cdot 10H_2O$ (10.0), $Na_2SiO_3 \cdot 9H_2O$ (1.5), NaMBT 50% solution (5.5), and NaOH (2.0)

[2] Inhibitors in (g/liter): $Na_3PO_4 \cdot 12H_2O$ (4.0), $NaNO_3$ (2.0), $Na_2B_4O_7 \cdot 10H_2O$ (6.0), $Na_2SiO_3 \cdot 9H_2O$ (1.0), NaMBT 50% solution (5.5), and NaOH (1.0)

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

**170 and $190^{o}C$ for propylene glycol and ethylene glycol based solutions, respectively.

may be available by then.

### 2. Gas Chromatographic Analyses

Aged glycol (both ethylene and propylene) were injected into a Varian series 2700 aerograph to obtain gas chromatographic data. Samples of the fresh glycol solutions were also injected to obtain baseline data. Unfortunately, all 34 aged glycol sample solutions obtained to date show no trace of any new species using this technique despite the pH changes noted in the study. The only logical explanation might be that no volatile organic compound exists in these samples. This most probably suggested that either organic acids formed as a result of glycol decomposition were totally evaporated, or even more dramatically, it indicated that glycol did not thermally decompose into simple organic acids. Instead, it might have polymerized to form non-volatile compounds which cannot be detected by a gas chromatographic analysis.

Additional attention will be focused on this aspect of our work during the remainder of this program. New techniques will have to be considered to precisely identify each product species in these aged glycol solutions.

## B. 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 temperature as well as sodium chloride concentration. The results are shown in Table II. These critical pitting potentials, which are reported in millivolts with respect to standard hydrogen electrode (SHE), are essentially information needed in the prevention of aluminum from pitting in aqueous ethylene glycol media.

It was found that the critical pitting potential of aluminum is a 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.

# TABLE II

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

| [NaCl] | $E_p$ (mV vs. SHE) | | | |
|---|---|---|---|---|
| | 25°C | 50°C | 70°C | 100°C |
| $10^{-4}$ | -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 |

Since protection of aluminum from pitting using zinc powder is achieved by lowering its potential to below $E_p$, it becomes more difficult as $E_p$ gets more negative. This implies that more zinc powder must be used to accomplish this purpose.

When plotting $E_p$ versus log $[Cl^-]$, we found that it yields a straight line at all four temperatures (see Figure 2). The following empirical expressions are obtained:

$$E_p \text{ (mV vs. SHE)} = -529 - 62.2 \log [Cl^-] \text{ at } 25^oC \qquad (1)$$

$$E_p \text{ (mV vs. SHE)} = -586 - 64.5 \log [Cl^-] \text{ at } 50^oC \qquad (2)$$

$$E_p \text{ (mV vs. SHE)} = -630 - 74.0 \log [Cl^-] \text{ at } 70^oC \qquad (3)$$

and

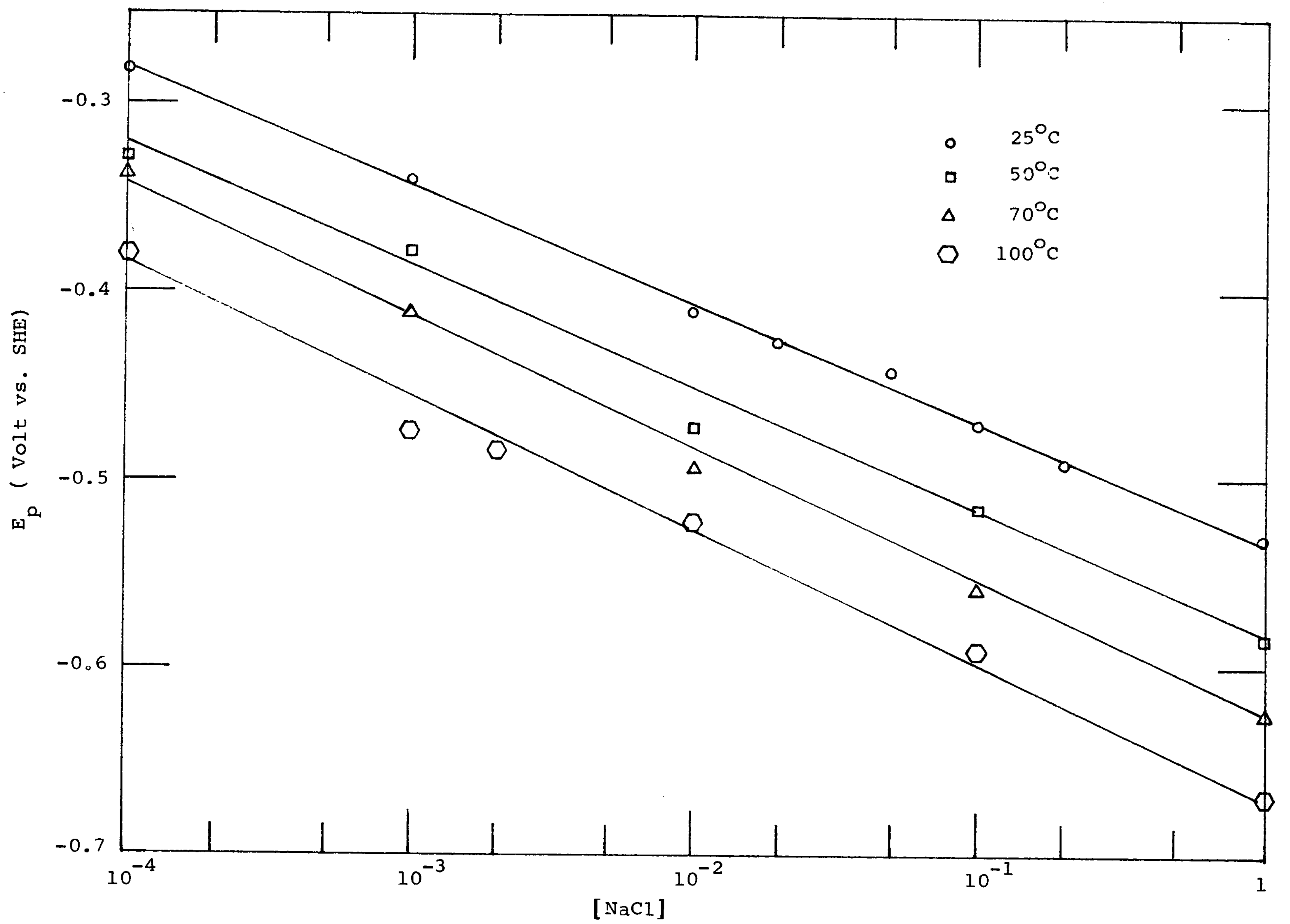
$$E_p \text{ (mV vs. SHE)} = -668 - 75.0 \log [Cl^-] \text{ at } 100^oC \qquad (4)$$

Similar results were reported by other researchers(3,8) for aluminum in pure aqueous NaCl solutions at $25^oC$:

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

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 1/2 of that in pure aqueous solutions.

Figure 2.



25°C
50°C
70°C
100°C
-0.3
-0.4
-0.5
-0.6
-0.7
$E_p$ ( Volt vs. SHE)
$10^{-4}$
$10^{-3}$
$10^{-2}$
$10^{-1}$
1
[NaCl]

## IV. CONCLUSIONS

1. When aged at elevated temperatures, both ethylene and propylene glycol solutions undergo chemical composition changes. This fact is reflected by a drop in solution pH as the aging process progresses.

2. Gas chromatographic analyses failed to support the common belief that glycols are thermally decomposed into organic acids. No new organic species can be detected using this technique. New techniques must be developed to monitor the glycol composition change as it aged.

3. The critical pitting potential ($E_p$) of aluminum in aqueous ethylene glycol solutions containing NaCl has been determined. It was found to obey the following:

$$E_p = E_p^o + S \log [Cl^-]$$

where $E_p^o$ and S are parameters which are temperature dependent.

(4) Critical pitting potential of aluminum becomes more negative as chloride concentration increases. It also becomes more negative as temperature rises for a fixed NaCl concentration.

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