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INHIBITOR ANALYSIS FOR A SOLAR HEATING AND COOLING SYSTEM

Prepared by

Department of Mechanical Engineering
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16. ABSTRACT

This report is a study of potential corrosion inhibitors for the NASA solar heating and cooling system which uses aluminum solar panels. The work is a continuation of the work performed in Supplement 1 of the NASA Grant 8025. This second phase of the research under this grant consisted of continued testing using the dynamic corrosion system developed in phase one, along with an economic analysis of the corrosion inhibitors tested in phases one and two. Very good progress was made in finding a suitable inhibitor for the system.

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I. INTRODUCTION

1.1 General Information

A solar heating and cooling system basically utilizes a solar energy collector, a large reservoir or water tank for thermal energy storage, heat exchangers for space heating and water heating, and normally an absorption cycle air conditioner for space cooling.

The water in the system is subject to temperatures in the approximate range of 200°F (93°C). In addition, the metallic construction materials are composed of both aluminum and steel with possibly small amounts of copper. The different materials, the high operating temperatures, and naturally the desire for long, maintenance-free operation necessitate analyzing the system for possible corrosion problems. One way to minimize corrosion problems is to add an inhibitor to the water.

An inhibitor is simply a substance which when added in a normally small amount to a corrosive solution reduces or eliminates corrosion problems in a system.

A study was begun in this area and is continuing with very good results under National Aeronautics and Space Administration Contract No. NSG-8025. The results presented in this report are through April 1977. The grant has been refunded and the studies will be completed by April 1978.

1.2 Objective and Scope

The objective of this research proposal is to continue the present studies in inhibitor analysis for a solar system. The continuing work to be done will be:

1. Rather than running a 7-day test on each inhibitor, run an extended test. That is, based upon the results of the initial 7-day tests, select the best inhibitors and run extensive tests (possibly as long as 6 months).

2. Test other inhibitors which may possibly work. These may be inhibitors we develop, some possibly suggested by NASA, or other commercial grades we think warrant testing.

3. Perform an economic evaluation of the cost of the tested inhibitors.

II. THEORY

2.1 Basic Corrosion Theory

Corrosion is defined as "the degradation of a material with resultant reduction in usefulness as far as application is concerned, because of inadvertent mechanical, chemical, or electro-chemical action or a combination of these."

There are eight basic forms of corrosion. They are galvanic corrosion, crevice corrosion, erosion corrosion, stress corrosion, uniform corrosion, intergranular corrosion, pitting corrosion, and selective leaching.

Galvanic corrosion is a form of corrosion based on electrochemical actions. It occurs when dissimilar metals or alloys are in contact with one another. Such galvanic couples create a difference of potential between the different areas of the structure. The greater the difference in potentials, the more severe the corrosion.

Crevice corrosion is intense localized corrosion caused by a shielded stagnant condition. This form of corrosion may occur if oxygen is available at some locations on the metal and is absent or used up in other localities. Crevices, joints, dead spots, or the bottoms of corrosion pits are particularly syscaptible to this form of attack because,even if air is present and the electrolyte is stirred, oxygen can only reach such places by slow diffusion. In a crevice or other region of imperfect mixing, where there is an insufficient supply of air, only the anodic reaction takes place and the metal corrodes. Away from the crevice, where air is more readily available; anodic and cathodic reactions take place and a film is formed.

Erosion corrosion is an accelerated rate of deterioration or attack of a metal because of relative movement between a corrosive medium and a metal surface. Erosion corrosion usually occurs in a pipe carrying a corrosive fluid at a very high Reynolds Number (turbulent flow). It can also occur in pipes which carry corrosive fluids at laminar flow speeds, but have sharp bends. The bends will cause turbulent conditions thus increasing the chance of erosion corrosion.

Stress corrosion is the acceleration of corrosion caused by the presence of an internal or external stress and a corrosive medium. This type of corrosion is found a great deal in cold-worked material where the distortion at the slip planes produced by the cold working causes accelerated precipitation and therefore a depletion of the solid solution of the alloy. When it occurs, normally the stress is below the yield strength.

Intergranular corrosion occurs in alloys where there is a potential difference between the grain boundary and the center of the grain. It is characterized by a localized attack between the grain boundaries with little corrosion damage to the grains themselves. It is commonly found in austenitic stainless steels (sensitization).

Pitting corrosion occurs when heterogeneties are present in the metal. Because of the difference in potential between the different points on the surface of the alloy, some of them corrode faster thus protecting the remaining areas and giving the surface a pitted appearance. It also occurs in metals protected by oxide film when a break or scratch occurs in the film causing a large cathode and a small anode effect.

Uniform corrosion is the most common type of corrosion. It takes place when the metal is completely homogeneous. The surface of the metal is evenly corroded and continues to dissolve, layer by layer.

Selective leaching is the selective removal of one element from a solid alloy by a corrosion process. Some forms of selective leaching are dezincification, the removal of zinc from brasses, and denickelfication, the removal of nickel from stainless steels or other nickel alloys.

2.2 Potential Corrosion Mechanisms in a Solar System

Of the eight forms of corrosion, there are three that will lead to corrosion problems in a solar heating and cooling system. They are uniform corrosion, galvanic corrosion because of the coupling of dissimilar metals, and pitting or crevice corrosion because the copper may dissolve in the solution and set up localized corrosion cells (anodes) on the aluminum panels. Erosion corrosion has not been a problem due to the low flow rates in the solar system.

III. CORROSION TEST SYSTEM AND OPERATION

Corrosion test results are only as accurate as the test system and procedures used to simulate the actual system. To produce useable results, the test system must duplicate as closely as possible the operation of the actual system. Further, the test procedure must be identical from test to test so that reproduceable results can be obtained. It is the author's opinion that the test system used and procedure followed do closely approximate an actual solar heating and cooling system.

3.1 Test Apparatus

In the test simulation of a solar heating and cooling system, a cartridge heater enclosed by an aluminum test coupon is used to simulate the solar panels. The aluminum tubing is 1100 series which is the same type used in the NASA panels. The cartridge heater which fit snugly in the tube provided the heat to the aluminum similar to the way the sun heats the actual solar panels. The cartridge heater and aluminum tube test coupon are then seated in a glass jacket. This glass jacket with inlet and exit spouts is mounted at a slight angle with the outlet spout on the high side. In the test system, the cartridge heater heats the aluminum which in turns heats the fluid. This is the same type phenomenon which occurs in an actual solar system. The sun's radiant energy heats the panels which in turn heat the fluid.

The storage basin is a 4 liter beaker which provides the fluid storage reservoir. The storage basin metal in the actual solar system is represented by a small piece of mild steel test coupon. The steel to aluminum area ratio is approximately 1:10. The galvanic coupling of the aluminum solar panels to the mild steel storage reservoir that exists in an actual solar system is accomplished by a copper wire attached to both the aluminum test coupon as well as the steel test coupon. Using a copper wire also simulates possible use of copper joints in the plumbing of an actual solar system.

The flow in the system is accomplished by a metaless (there are no metal pump components) pump. The flow rate is 50 ml per minute. The pump begins flowing at the same time as the cartridge heater begins heating. They both run for 9 hours per day which is the approximate time that sun energy heats the panels in an actual solar system. The reservoir which contains 3 liters of test solution (test solution is covered in section 3.2) is maintained at temperature when the cartridge heater isn't heating by a calibrated hot plate. Power to both the hot plate and to the cartridge heaters is provided through variacs. This allows closer temperature control. The base temperature in the storage basin is always maintained at a minimum 180°F (87°C) and once the cartridge heater is turned on, the temperature increases to 200°F (93°C) steady state for day time operation. The entire system is closed as is the case in an actual solar system. The system is on an electrical timer and the variac power is turned off and on by relays. A list of major components and a system schematic are included in the appendix.

3.2 Test Solution

Water composition varies from location to location. Because of this and in the interest of reproduceability, a synthetic water is used for testing. The water is made in the lab under close tolerances so that the chemical composition will not vary from test to test. The synthetic water is made by adding the following to distilled water.

300 mg/l	$CaCl_2 \cdot 2H_2O$
100 mg/l	$MgSO_4$
25 mg/l	NaCl
100 mg/l	Na_2SO_4
75 mg/l	$NaHCO_3$

To this synthetic water the correct proportions of various inhibitors were added.

3.3 Test Procedure

Care was taken so that all tests were conducted as nearly identical as possible. The procedure is as follows:

1. Sample preparation
   a. The aluminum and steel test coupons are sanded with 120 grit emory paper. They are then washed and air dried.
   b. The area of the aluminum and steel test coupons were computed to the nearest 0.001 square inch.
   c. The aluminum and steel test coupons are degreased with acetone.
   d. The aluminum and steel test coupons are each weighed to an accuracy of 0.01 mg.
   e. The coupons are placed in a dessicator until the test is to begin.
2. Test solution preparation
   a. The chemicals used to add to the distilled water were weighed to an accuracy of 0.01 mg.

b. The chemicals were then added to the three liters of distilled water.

c. The correct amount of inhibitor was measured and added to the synthetic water.

3. Set up all apparatus and test samples as shown in the schematic of the system in the appendix.
4. The test solution is added to the storage basin. The special top is then sealed on the beaker.
5. All connections are sealed to close the system.
6. The electricity to the system is turned on. The test is monitored, but the entire test is controlled through timers, relays, and variacs.
7. The test is continued for the desired test time.
8. The aluminum and steel test coupons are removed from the system and cleaned. Cleaning is performed with mild soap and a toothbrush. They are then dried and placed in the dessicator.
9. The following day the test coupons are again cleaned by the same method outlined in number 8.
10. The test coupons are again weighed in order to be able to compute the weight lost by the coupons during the test.
11. The corrosion rate is then computed with the following equation,

$$\text{Corrosion Rate} = \frac{534 \times W}{D \times A \times T}$$

where
W = Weight loss in mg
A = Exposed area in square inches
D = Density in grams per cubic centimeter
T = Test time in hours

By using this equation, the corrosion rate is computed in mils per year.

12. The entire system is cleaned and flushed with distilled water, then allowed to dry.
13. The pump is flushed with distilled water and the flowrate checked so that it is still operating at 50 ml per minute.

IV. RESULTS

4.1 Short Term Testing

All inhibitors noted in the inhibitor survey conducted in the first final report on the research were tested. All short term testing consisted of 7-day tests. The best 7-day test results were obtained from Hercules' CR 408 (Southern Test No. 10), Pro-Chem's 7131 (Southern Test No. 22), a special inhibitor developed by General Motors (Southern Test No. 29), and sodium chromate (Southern Test No. 28). The best overall performance was achieved by using 1000 ppm of sodium chromate. In 7-day testing, there was zero corrosion noted on the aluminum and only a 0.65 mpy corrosion rate noted on the steel.

All short term test results and long term test results are shown in Table 1.

4.2 Long Term Tests

Five 60-day tests were conducted. The inhibitors tested were: (1) a control with no inhibitor (Southern Test No. 26), (2) Hercules' CR 408 (Southern Test No. 25), (3) Sodium Chromate (Southern Test No. 30), (4) Hercules' CR 408 (Southern Test No. 32), and (5) The inhibitor developed by General Motors (Southern Test No. 33).

Longer testing resulted in a pitting or crevice type of attack. This severe attack did not occur in the short term testing due to the short test duration. It occurred in all inhibitors tested except the sodium chromate. It is anticipated that the pitting or crevice attack can be reduced by varying the concentrations of the inhibitors. However, testing to date indicates that the sodium chromate is the best inhibitor tested. There was no crevice or pitting attack and the overall corrosion rate was 0.12 mpy for the aluminum and 1.77 mpy for the steel. Long term test results are included in Table 1.

4.3 Economic Analysis of the Tested Inhibitors

An economic analysis of the tested inhibitors was performed. The data includes each inhibitor's unit cost, concentration tested, amount required for a 5000 gallon system, and the cost for inhibiting a 5000 gallon system. Data was supplied by the companies and are supposed to reflect the retail cost. All data is compiled in Table 2.

TABLE 1

Test No.	Inhibitor	Concentration (ppm)	Manufacturer	Al. Corrosion (mpy)	Steel Corrosion (mpy)	Remarks
2	NONE	--------	--------	13.92	50.15	First complete test
4	NONE	--------	--------	2.61	30.93	Pump problem
5	NONE	--------	--------	6.66	21.66	1 week
6	AF 518	100	Hercules	7.34	26.70	1 week
7	CR 408	250	Hercules	1.06	7.73	1 week
8	CR408/AF518	250/50	Hercules	4.36	11.30	1 week
9	X-19711-14	5000	Hercules	14.39	26.40	1 week
10	CR 408	500	Hercules	0.29	3.39	1 week
11	NONE	--------	--------	5.97	23.81	1 week
12	X-19711-14	5000	Hercules	3.94	23.24	1 week
13	CR481/X-19711	2000/50	Hercules	3.99	23.35	1 week
14	CR 481	2000	Hercules	1.33	22.19	1 week
15	Amine	2000	Mogul	52.96	125.83	1 week
16	1366	5000	Watcon	32.75	21.43	1 week
17	1805	50	Alox	2.36	18.45	1 week

CORROSION TEST RESULTS FOR A SOLAR HEATING AND COOLING SYSTEM

TABLE 1 (Continued)

Test No.	Inhibitor	Concentration (ppm)	Manufacturer	Al. Corrosion (mpy)	Steel Corrosion (mpy)	Remarks
18	Nacap 11-10-D	0.4% by vol.	Vanderbilt	13.42	14.24	1 week
19	Nacap 11-10-D	0.4% by vol.	Vanderbilt	11.91	10.67	1 week
20	WSSG-200	5000	Dynamic	15.03	25.29	1 week
21	WS-142	2000	Mogul	6.53	7.56	1 week
22	7131	2% by volume	Pro-Chem	1.30	0.77	1 week
23	41-LB-6026	4500	Nalco	13.80	0.77	1 week
24	37	6000	Nalco	23.59	0.58	1 week
25	CR 408	500	Hercules	0.95	6.24	2 months
26	NONE	----------	-----------	1.41	19.23	2 months
27	General Motors	* Below	G M	7.20	1.29	1 week
28	Sodium Chromate	1000	-----------	0	0.65	1 week
29	General Motors	* Below	G M	0	12.80	1 week
30	Sodium Chromate	1000	-----------	0.12	1.77	2 months
31	Thermofluid 17	50% by volume	Union Carbide	7.[illegible]1	0.79	1 week
32	CR 408	2000	Hercules	2.45	7.04	2 months
33	General Motors	* Below	G M	1.12	0	2 months

* 1000 ppm Sodium Nitrate   2000 ppm Sodium Phosphate   2500 ppm Sodium MBT

3000 ppm Sodium Borate   1000 ppm Sodium Silicate   1000 ppm Sodium Hydroxide

TABLE 2
Economic Analysis of the Tested Inhibitors

Inhibitor	Unit Cost	Available in	Concentration	Amt for 5000 Gal System	Cost for 5000 Gal System	Discounts
Pro-Chem, Inc. #7131	$3.50/Gal	55 Gal Drum	2% by Vol. (20000 ppm)	100 gals	$350.00	
Mogul Corporation Mogul WS - 142	.95/lb	450 lb Drum	2000 ppm	5.82 lbs	5.53	For 3-12 Drums - 1/2¢ 12+ Drums - 2¢
Hercules, Inc. CR 408 AF 518 CR 481	0.57/lb 0.54/lb 0.39/lb		2000 ppm 100 ppm 2000 ppm	5.82 lbs 0.29 lbs 5.82 lbs	3.32 0.15 2.27	Over 40 Drums - 1¢/lb
Watcon, Inc. Watcon, 1366	3.60/Gal		5000 ppm	25 gals	90.00	
Alox Corp. Alox 1805	0.56/lb	55 Gal Drum	50 ppm	0.15 lbs	0.08	Over 2000 lbs - 4¢/lb
RT Vanderbilt, Inc. NACAP	0.45/lb	575 lb Drum	0.4% by Vol. (4000 ppm)	1.16 lbs	5.24	(Also available in 50 lb pails @ 73¢/lb)
Rust-Lick, Inc. (Formerly Dynamic Chem Co.)	3.50/gal	55 Gal Drum	5000 ppm	25 gals	87.50	
Nalco Chemical Co. #37 #41L	1.09/lb 0.876/lb	55 Gal Drum 50 lb Bag	6000 ppm 4500 ppm	17.47 lbs 13.10 lbs	19.04 11.48	Over 4 Drums - 5¢/lb Over 2000 lbs-16.9¢/lb
Union Carbide Thermofluid 17	$3.65/Gal	55 Gal Drum	50% by Vol. (500,000 ppm)	2500 gals	$9125.00	Over 40 Drums - 15¢ Over 80 Drums - 25¢ (Minimum Order-20 Drums)
Sodium Chromate (Na_2CrO_4)	5.72/lb	1 lb sx.	1000 ppm	2.91 lbs	16.66	Also available in 25 lb sxs.

V. CONCLUSIONS

The following list of conclusions are in the author's opinion the significant findings to date.

1. There appear to be commercially available inhibitors that can adequately protect a solar heating and cooling system from corrosive attack.
2. The test system designed to simulate a solar heating and cooling system works very well and very closely approximates an actual solar system.
3. Without using an inhibitor, the corrosion rate was found to be approximately 6.3 mils per year for aluminum and 22.7 mils per year for steel.
4. The best inhibitor found in the short term testing (7-day tests) was sodium chromate. There was zero corrosion noted on the aluminum and only a 0.65 mpy corrosion rate noted on the steel.
5. Long term testing (60-day tests) resulted in a pitting or crevice type of attack. This severe attack did not occur in the short term testing due to the short test duration. It occurred in all long term tests with the exception of the sodium chromate.
6. The best inhibitor found in the long term testing (60-day tests) was sodium chromate. There was no crevice or pitting attack and the overall corrosion rates was 0.12 mpy for aluminum and 1.77 mpy for steel.

VI. FUTURE STUDY AREAS DURING THE THIRD YEAR OF TESTING

The following areas will be studied during the third supplement of NASA grant NSG-8025.

1. Continue and expand the long term testing.
2. Resurvey the inhibitor manufacturers to see if any new inhibitors have been developed since the original survey in 1975.
3. Test any new inhibitors found in the new survey.

VII. APPENDIX

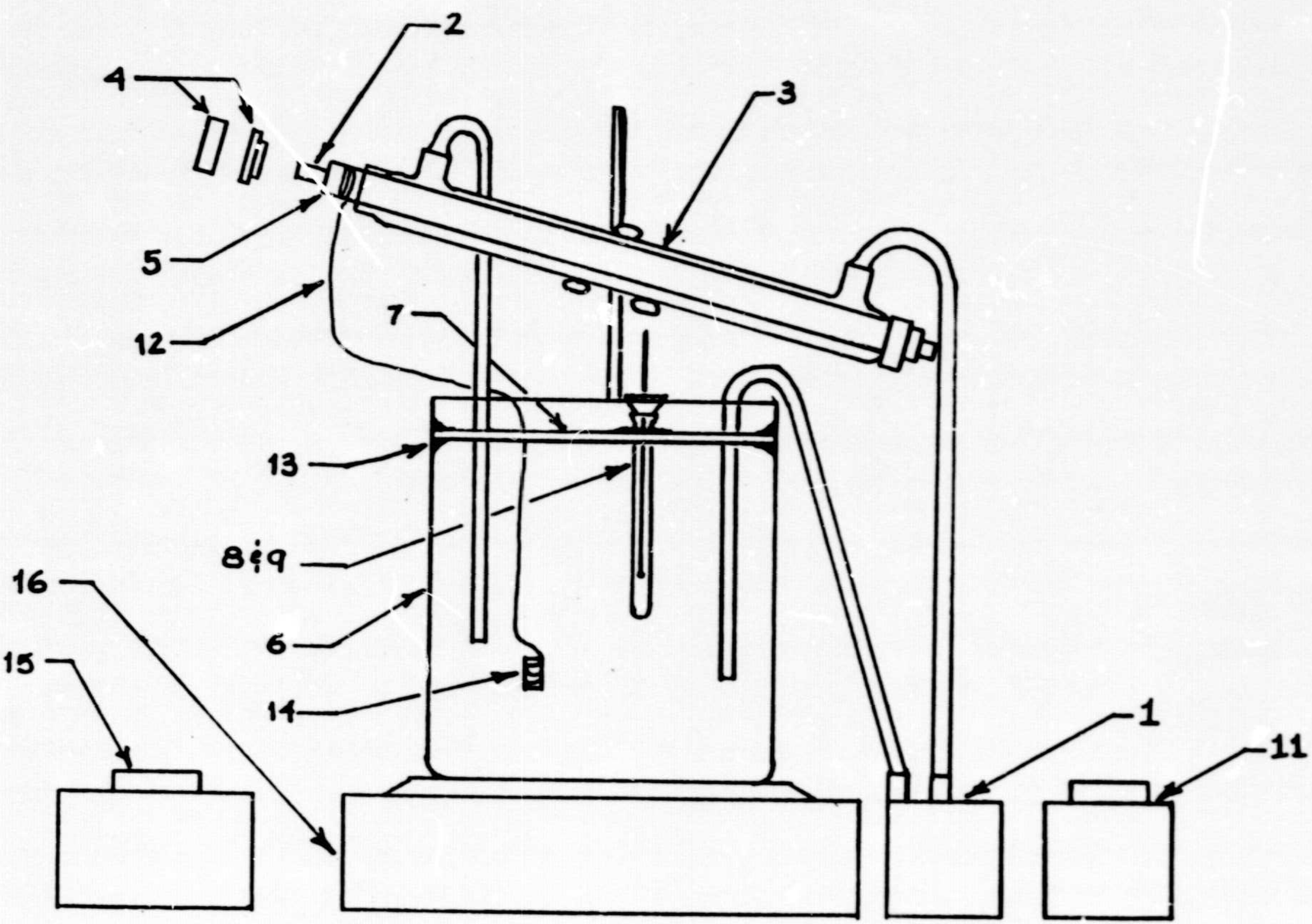
7.1 Equipment List (Equipment numbers correspond to numbers on test system schematic.)

Item	Source
1. Pump March Nettering Pump Metal-less construction Model 210-5	March Mfg. Co. 1819 Pickwide Ave. Glenview, Ill. 60025
2. Cartridge Heater 3/8 inch OD x 12 inch length 120 volts - 600 watts Type A leads Stainless Steel Shaft	Fast Heat Mfg. Co. 3333 North Knox Ave. Chicago, Ill. 60641
3. Glass Jacket LG-18003-A Liebig Condenser Jacket 250mm length	Lab Glass, Inc. North West Blvd. Vineland, NJ 08360
4. Nut and Washer LG-18003-A	Lab Glass, Inc.
5. Heat Transfer Tube Seamless Aluminum Tubing (1100 Series) .500 inch OD ± .005 .380 inch ID ± .003 - .000	Alcoa
6. Basin 4 liter glass beaker	Lab Glass, Inc.
7. Top Plexiglass top to fit inside beaker and rest on stop made of hardened silicon sealant ID of beaker - .2 inch	
8. Test Tube	Lab Glass, Inc.
9. Thermometer	Lab Glass, Inc.
10. Electrical Switch	
11. Variac To Cartridge Heater	Lab Glass, Inc.
12. Copper Wiring	
13. Sealant	

14. **Steel Coupon**

15. **Variac To Hot Plate** Lab Glass, Inc.

16. **Hot Plate**



7.2 Test System Schematic