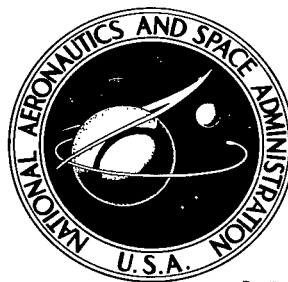


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CORROSION INHIBITORS FOR SOLAR HEATING AND COOLING SYSTEMS

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16. ABSTRACT Problems dealing with corrosion and corrosion protection of solar heating and cooling systems are discussed. A test program was conducted to find suitable and effective corrosion inhibitors for systems employing either water or antifreeze solutions for heat transfer and storage. Aluminum-mild steel-copper-stainless steel assemblies in electrical contact were used to simulate a multimetallic system which is the type most likely to be employed. Several inhibitors show promise for this application.			
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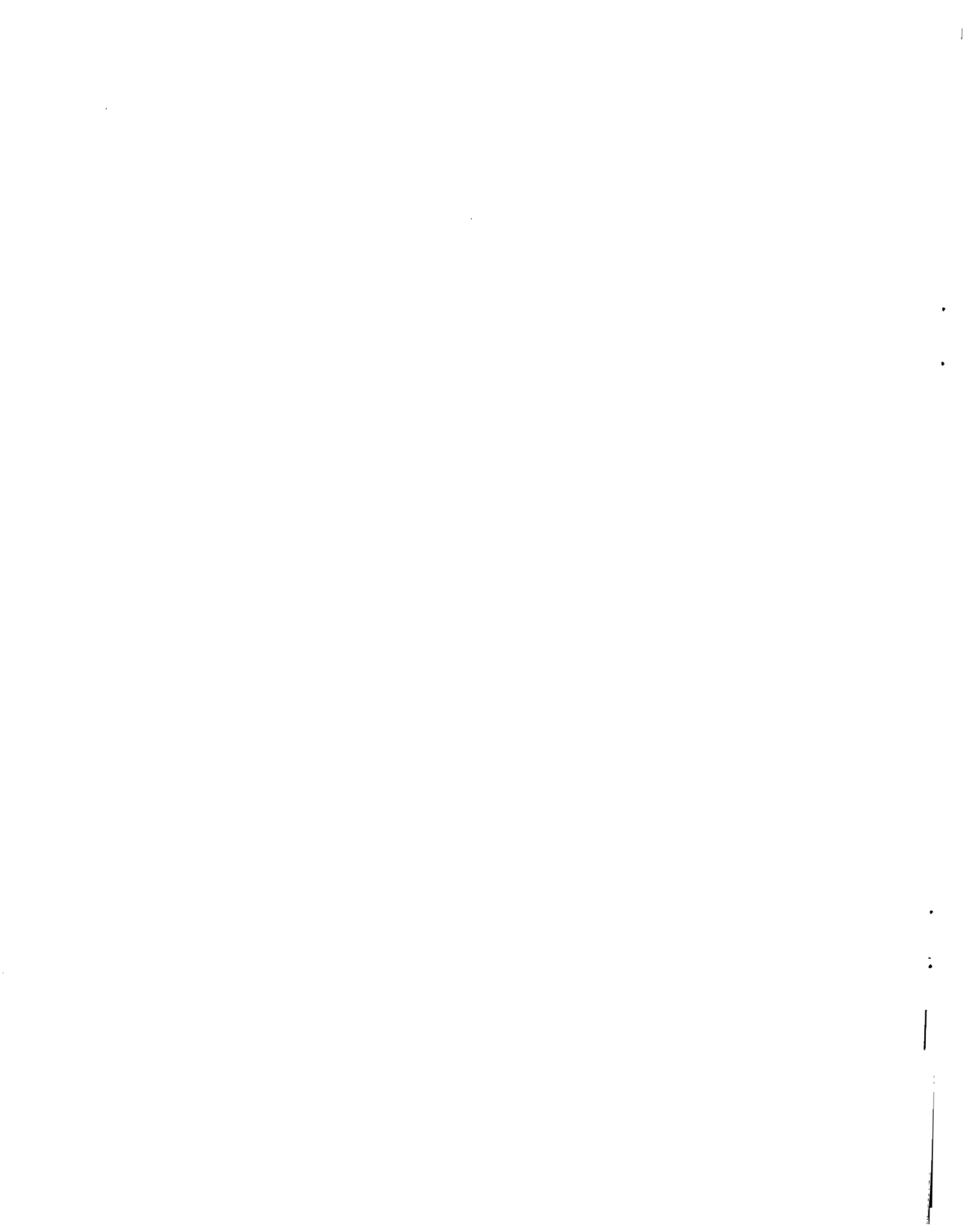


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CORROSION INHIBITORS FOR SOLAR HEATING AND COOLING SYSTEMS

INTRODUCTION

Compatibility of heat transfer and heat storage fluids with the materials of construction is a prerequisite to insuring efficient operation and long life for solar heating and cooling units as well as other similar systems. Water is one of the most promising heat transfer and heat storage fluids because of a combination of physical properties, availability, and cost. Unfortunately most waters are corrosive to aluminum and steel, the two metals which probably will be used extensively in solar heating and cooling systems. The most practical and economical method of combatting corrosion in this type of system is the use of corrosion inhibitors. Protecting such a system with corrosion inhibitors may prove extremely difficult because off-the-shelf items such as valves, controllers, etc. will be used and will result in a variety of metals such as mild steel, aluminum, stainless steel, and copper being in contact with the fluid. In addition, part of the unit will be operated at a relatively high temperature [93°C (200°F)] if the system is used for cooling. No toxic or polluting material may be used in solar heating systems which complicates the problem further by limiting the choice of chemicals that may be used in formulating an inhibitor.

TEST PROCEDURE

A survey of inhibitors recommended for automotive coolants was conducted because of the similarity of operation (multimetallic and high temperature). Several inhibitors were selected from the survey and some simpler inhibitors were formulated for evaluation. Only inhibitors whose constituents were considered nontoxic and nonpolluting in small amounts were used. The composition of the test inhibitors is given in Table 1.

Small 2.5 by 7.5 cm specimens were sheared from sheets of 1100 aluminum, 1010 steel, and 321 stainless steel, and 1.9 by 7.5 cm specimens were sheared from electrolytic tough pitch copper. The sheet thicknesses ranged from 0.9 mm for the steel to 3.125 mm for the aluminum. All the specimens were deburred and cleaned in a hot alkaline bath (aluminum in

Enbond NE-6 and the others in Enbond S-64). The aluminum specimens were etched in a 10 percent nitric acid-2 percent hydrofluoric acid solution and desmuted in 40 percent nitric acid. The mild steel and stainless steel specimens were cleaned in 20 percent hydrochloric acid and the copper in 40 percent nitric acid.

Test assemblies were made by drilling a small hole in one end of each specimen, inserting an 18-8 stainless steel machine screw (size 10-32, 1-1/8 in. long) through the hole in the 1100 aluminum alloy specimen, and securing it with a stainless steel nut. Steel, copper, and stainless steel specimens were added in sequence to the screw, and a stainless steel nut secured finger tight was placed between each specimen to act as a separator and to insure electrical contact (Fig. 1).

The assemblies were immersed in 450 ml of the respective solutions contained in 500 ml Erlenmeyer flasks covered with loosely fitting, flat head, glass stoppers. One test was conducted at room temperature and a second at 82°C (180°F). All the test assemblies were removed from the solutions and placed in empty covered flasks each working day for 8 h. This procedure was used to simulate a system drained at night during the winter to prevent freezing. The specimens were visually inspected each working day, and the solution level was maintained by additions of distilled water to insure constant solution concentration. After 1 year of exposure, the assemblies were removed, disassembled, cleaned, and weighed. The specimens were cleaned according to ASTM G1-72, "Preparing, Cleaning, and Evaluating Corrosion Test Specimens," paragraphs 5.1, 5.2, 5.7.2, and 5.8.2.

RESULTS AND DISCUSSION

Since perforation of solar heating components will make the system inoperative, the type and depth of attack were the major factors used in the corrosion evaluation. The appearance of all test specimens is shown in Figures 2 and 3, and a description of the condition of the aluminum and mild steel specimens is given in Tables 2 and 3. The stainless steel and copper specimens were not included in Tables 2 and 3 because the stainless steel specimens were unaffected and the copper specimens were only tarnished (maximum calculated corrosion rate of less than 0.003 mm/year). The terms mild, moderate, and severe in the tables refer more to the depth of attack than to the number of pits or to the area affected by corrosion. In addition, attack limited to the edges, vicinity of the screw connector, or the bottom edge only was considered but was

not given the same degree of importance as randomly scattered attack. Many components would not have an edge in contact with the fluid or be in such intimate contact with dissimilar metal as was present in the test couple. Most components such as pipe and tubing can tolerate considerably more edge attack without perforation than normal pitting through the walls.

Weight loss is included in Tables 4 and 5 but it was used only in rating corrosion of specimens for which the general pattern of attack was similar and the frequency of pitting or area affected by non-uniform attack were approximately the same. Weight loss can be very misleading as illustrated by the aluminum specimens in solution 3 (Table 4) and solution 12 (Table 5). These two specimens received a more favorable rating than other specimens that lost less weight because the corrosion rate was not excessive (calculated rate of 0.03 to 0.05 mm/year) and there was no significant pitting.

The final pH values of the elevated and room temperature solutions were similar although aluminum and mild steel suffered considerably more corrosion in the hot solutions (Tables 4 and 5). It was surprising that some of the most effective corrosion inhibitors for aluminum were highly alkaline (pH 11.5, solutions 1 and 4). Solutions that are moderately or highly alkaline (pH 10 or higher) are normally corrosive to aluminum.

Several freshly prepared inhibited solutions (mainly Nos. 5 and 7) contained a flocculent precipitate as may be seen in Figure 4. However, it is doubtful if this precipitate would interfere with the operation of most systems. The appearance of the solutions after exposure is shown in Figure 5.

Evaluation of the corrosion inhibitors was based on the corrosion protection afforded aluminum and mild steel because neither stainless steel or copper suffered any significant corrosion in any of the solutions, including the uninhibited ones used as standards for comparison. This indicates that the most corrosion resistant system would be one constructed of stainless steel, copper, or a combination of the two. The cost of such a system, however, will no doubt be prohibitive. The evaluation scheme for the inhibitors was based on three major categories according to exposure temperature, and these were further divided into three categories based on protection afforded to aluminum, steel, or a combination of the two (Table 6). The reason for this latter category is that the aluminum components may be corrosion critical in some systems, mild steel components may be corrosion critical in others, but in many systems it may be difficult to determine which components are critical and the inhibitor must protect aluminum and steel equally.

CONCLUSIONS

As may be seen in Table 6, inhibitors 1, 3, and 5 are acceptable based on protection of aluminum and steel at elevated temperature and 1, 5, and 12 are acceptable at room temperature. Conditions in solar heating and cooling systems will range from areas of minimum to areas of maximum temperatures; for example, the solar collectors will be the hottest during the heating cycle. Thus inhibitors 1 and 5 are the most effective because they protected aluminum and steel at room and elevated temperature. If the steel components are not corrosion critical, inhibitors 4, 1, 3, 5, and 12 may give adequate protection, and inhibitors 8, 1, 5, and 7 may be used if no aluminum parts are corrosion critical. Surprisingly, sodium chromate is not a very effective inhibitor under these test conditions. Inhibitor 6 is rated compatible under all test conditions, although at elevated temperature the aluminum specimen suffered pronounced pitting along the bottom edge. It should be noted that these tests were conducted under quiescent conditions with the specimens immersed in the solution, and the effects of fluid flow and liquid to metal heat transfer were not evaluated.

TABLE 1. CORROSION INHIBITORS

1.	1.0 NaNO ₃ , 2.0 Na ₃ PO ₄ · 12H ₂ O, 2.5 NaMBT, 3.0 Na ₂ B ₄ O ₇ , 1.0 Na ₂ SiO ₃ · 9H ₂ O, 1.0 NaOH.
2.	4.0 Na ₃ PO ₄ · 12H ₂ O, 2.0 Na ₂ SiO ₃ · 9H ₂ O, 4.0 NaMBT.
3.	1.5 NaNO ₃ , 2.0 Na ₃ PO ₄ · 12H ₂ O, 2.5 NaMBT, 4.0 Na ₂ B ₄ O ₇ .
4.	1.5 NaNO ₃ , 2.5 Na ₃ PO ₄ · 12H ₂ O, 4.0 NaMBT, 2.0 Na ₂ SiO ₃ · 9H ₂ O.
5.	1.4 Na ₂ HPO ₄ , 2.4 MBT, 6.2 Na ₂ B ₄ O ₇ : Source - 15.0 Cooling System Inhibitor, Federal Specification 0-1-490A.
6.	50 volume percent "Permanent Type Anti-Freeze" (ethylene glycol base).
7.	20.0 DuPont "Anti-Rust," an automotive coolant inhibitor.
8.	12.0 NaC ₇ H ₅ O ₂ , 1.0 NaNO ₂
9.	1.0 Na ₂ CrO ₄
10.	Uninhibited test water.
11.	50 volume percent uninhibited ethylene glycol.
12.	Same as No. 1 without the NaOH.

All concentrations in grams per liter except as noted.

NaNO₂ - sodium nitrite

NaNO₃ - sodium nitrate

Na₂B₄O₇ - sodium borate

Na₂SiO₃ - sodium silicate

Na₂HPO₄ - disodium phosphate

MBT - mercaptobenzothiazole

NaMBT - sodium mercaptobenzothiazole (50% solution).

Na₃PO₄ - trisodium phosphate

NaC₇H₅O₂ - sodium benzoate

Na₂CrO₄ - sodium chromate

NaOH - sodium hydroxide

TABLE 2. VISUAL DESCRIPTION OF CORROSION OF
ELEVATED TEMPERATURE TEST SPECIMENS

<u>Inhibitor</u>	<u>Alloy</u>	<u>Visual Description</u>
1.	Al -	One deep pit on the bottom edge and several shallow pits on the bottom and one side edge.
	Fe -	Mild nonuniform attack mainly on the bottom edge.
2.	Al -	Scattered areas of moderate nonuniform attack with deep pits around the screw.
	Fe -	Scattered areas of mild to moderate nonuniform attack.
3.	Al -	No visible corrosion. Specimen coated with adherent black film.
	Fe -	Mild nonuniform attack in vicinity of the screw with moderate attack on bottom edge.
4.	Al -	No visible attack.
	Fe -	Scattered moderate to severe pitting and nonuniform attack.
5.	Al -	Scattered areas of mild nonuniform attack. Specimen coated with adherent black film.
	Fe -	Scattered areas of mild nonuniform attack.
6.	Al -	Mild to moderate pitting of edges with severe pitting of bottom edge.
	Fe -	Scattered areas of mild to moderate nonuniform attack.
7.	Al -	Scattered deep pitting mainly at bottom and around screw.
	Fe -	Mild nonuniform attack concentrated at edges.
8.	Al -	Moderate nonuniform attack.
	Fe -	No visible corrosion.
9.	Al -	Several deep pits around screw.
	Fe -	Several scattered moderate to deep pits.
10.	Al -	Scattered areas of deep pitting.
	Fe -	Severely etched plus nonuniform attack.
11.	Al -	No visible attack. Specimen coated with loosely adherent dark film.
	Fe -	Severely etched, 50 percent weight loss.
12.	Al -	Moderately deep pits on all edges.
	Fe -	Moderate nonuniform attack with severe attack of bottom edge.

NOTE: The terms mild, moderate, and severe refer mainly to depth of attack.

TABLE 3. VISUAL DESCRIPTION OF CORROSION OF ROOM TEMPERATURE TEST SPECIMENS

<u>Inhibitor</u>	<u>Alloy</u>	<u>Visual Description</u>
1.	Al - Fe -	No visible corrosion. Several shallow pits on bottom edge.
2.	Al - Fe -	Several deep pits around screw and on bottom edge. No visible corrosion.
3.	Al - Fe -	No visible corrosion. Moderate nonuniform attack with severe attack of bottom edge.
4.	Al - Fe -	No visible corrosion. Mild nonuniform attack with one top corner edge corroded away.
5.	Al - Fe -	No visible corrosion. No visible corrosion.
6.	Al - Fe -	No visible corrosion. No visible corrosion.
7.	Al - Fe -	Deep pitting around screw and on bottom edge. Scattered mild nonuniform attack.
8.	Al - Fe -	Several deep pits on bottom edge and one near screw. No visible corrosion.
9.	Al - Fe -	One top corner severely exfoliated. Bottom edge severely pitted.
10.	Al - Fe -	Moderate nonuniform attack on edges and around screw. Moderate nonuniform attack with bottom edge corroded away.
11.	Al - Fe -	Scattered pits moderately deep. Nonuniform attack moderately deep.
12.	Al - Fe -	The only visible corrosion was several spots of mild attack on the edges. No visible corrosion.

NOTE: The terms mild, moderate, and severe refer mainly to depth of attack.

TABLE 4. ELEVATED TEMPERATURE CORROSION TEST DATA

Solution No.	pH		Alloy	Weeks to First Visual Attack	Description of Corrosion	Weight Loss (mg)
	Original	Final				
<u>Corrosive Water</u>						
1	11.5	9.5	Al	40	P (be)	26
			Fe	5	C (be)	83
2	11.7	9.5	Al	3	C (sc)	552
			Fe	16	C (sc)	385
3	9.4	8.7	Al	-	N	749
			Fe	16	C (vc, sc)	279
4	11.6	9.4	Al	-	N	0
			Fe	2	C, P (sc)	1293
5	9.4	8.7	Al	16	E, C (sc)	292
			Fe	40	C (sc)	385
7	9.6	9.8	Al	1	P (sc, be major)	251
			Fe	2	C (sc)	595
8	8.1	8.8	Al	1	P, C (sc)	309
			Fe	-	N	5
9	9.0	9.2	Al	2	F (vc)	229
			Fe	2	P (sc)	268
12	9.7	7.8	Al	52	E, P (ae)	300
			Fe	2	C (be major)	1609
10	8.2	5.0	Al	5	P (sc)	436
			Fe	2	C (sc)	3172
<u>Corrosive Water and Glycol (50-50 Mixture)</u>						
6	10.1	8.6	Al	16	P(ae, be major)	126
			Fe	3	C (sc)	197
11	8.4	5.1	Al	-	N	0
			Fe	2	E	5662

C - Nonuniform attack
 E - Etched
 N - No visible corrosion

P - Pitted
 ae- all edges
 be- bottom edge

sc - scattered
 vc - vicinity of screw

TABLE 5. ROOM TEMPERATURE CORROSION TEST DATA

Solution No	pH		Alloy	Weeks to First Visual Attack	Description of Corrosion	Weight Loss (mg)
	Original	Final				
<u>Corrosive Water</u>						
1	11.5	9.3	Al	-	N	0
			Fe	16	P (be)	14
2	11.7	9.2	Al	1	P (vc, be major)	175
			Fe	-	N	0
3	9.4	9.3	Al	-	N	24
			Fe	2	C (be major)	658
4	11.6	9.0	Al	-	N	0
			Fe	3	C (sc)	445
5	9.4	8.5	Al	-	N	22
			Fe	-	N	0
7	9.6	9.7	Al	1	P (vc, be)	325
			Fe	1	C (sc)	22
8	8.1	9.0	Al	1	P (be)	239
			Fe	-	N	0
9	9.0	9.4	Al	1	X	217
			Fe	1	P (be)	86
12	9.7	8.9	Al	*	*	300
			Fe	-	N	24
10	8.2	9.4	Al	16	P, C (ae, vc)	46
			Fe	1	C (be major)	1400
<u>Corrosive Water and Glycol (50-50 Mixture)</u>						
6	10.1	8.9	Al	-	N	0
			Fe	-	N	0
11	8.4	6.4	Al	5	P	127
			Fe	1	C	1495

* The only corrosion was several spots of mild attack on the edge.

C - Nonuniform attack	P - Pitted	be - bottom edge
E - Etched	X - Exfoliated	sc - scattered
N - No visible corrosion	ae - all edges	vc - vicinity of screw



TABLE 6. RATING OF THE CORROSION INHIBITORS^a

Elevated Temperature			Room Temperature			Combination		
Al	Steel	Both ^c	Al	Steel	Both ^c	Al ^c	Steel ^c	Both ^c
4 ^b	8 ^b	1 [?]	4 ^b	8 ^b	1	4	8	1
3 ^b	1 ^b	3	1 ^b	2 ^b	5	1	1	5
1 ^b	9 ^b	5	3 ^b	5 ^b	12	3	5	
12 ^b	5 ^b		5 ^b	1 ^b		5	7	
5 ^b	3 ^b		12 ^b	12 ^b		12		
9	7 ^b		2	7 ^b				
8	2		9	9				
2	4		8	4				
7	12		7	3				
6 ^d	6 ^d	6 ^d	6 ^d	6 ^d	6 ^d	6 ^d	6 ^d	6 ^d

- NOTES:
- The inhibitors are listed in descending order according to their effectiveness.
 - These are the only inhibitors that were considered acceptable in each category.
 - Only those inhibitors that were considered acceptable in the previous categories are rated.
 - This inhibitor is acceptable in all categories but is listed separately because the solution is glycol-water (see Table 1).

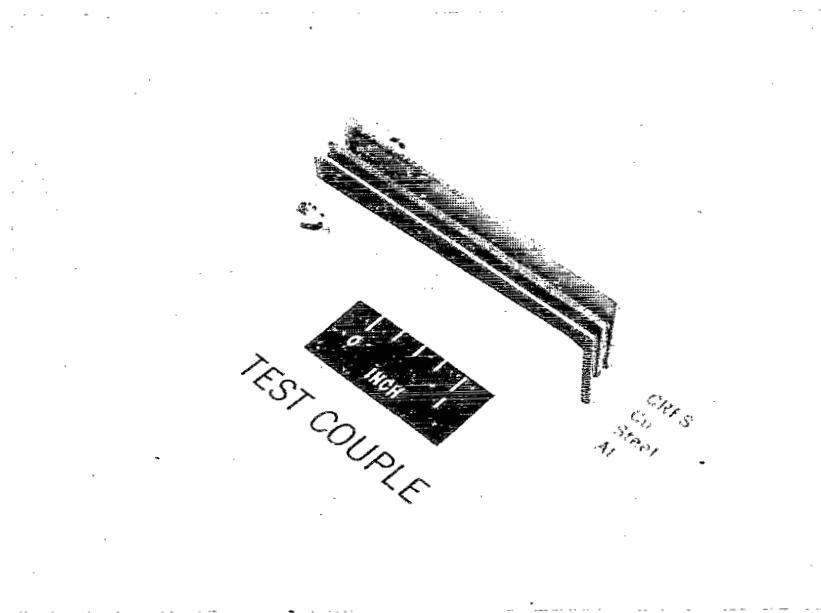


Figure 1. Test assembly and method of exposure.

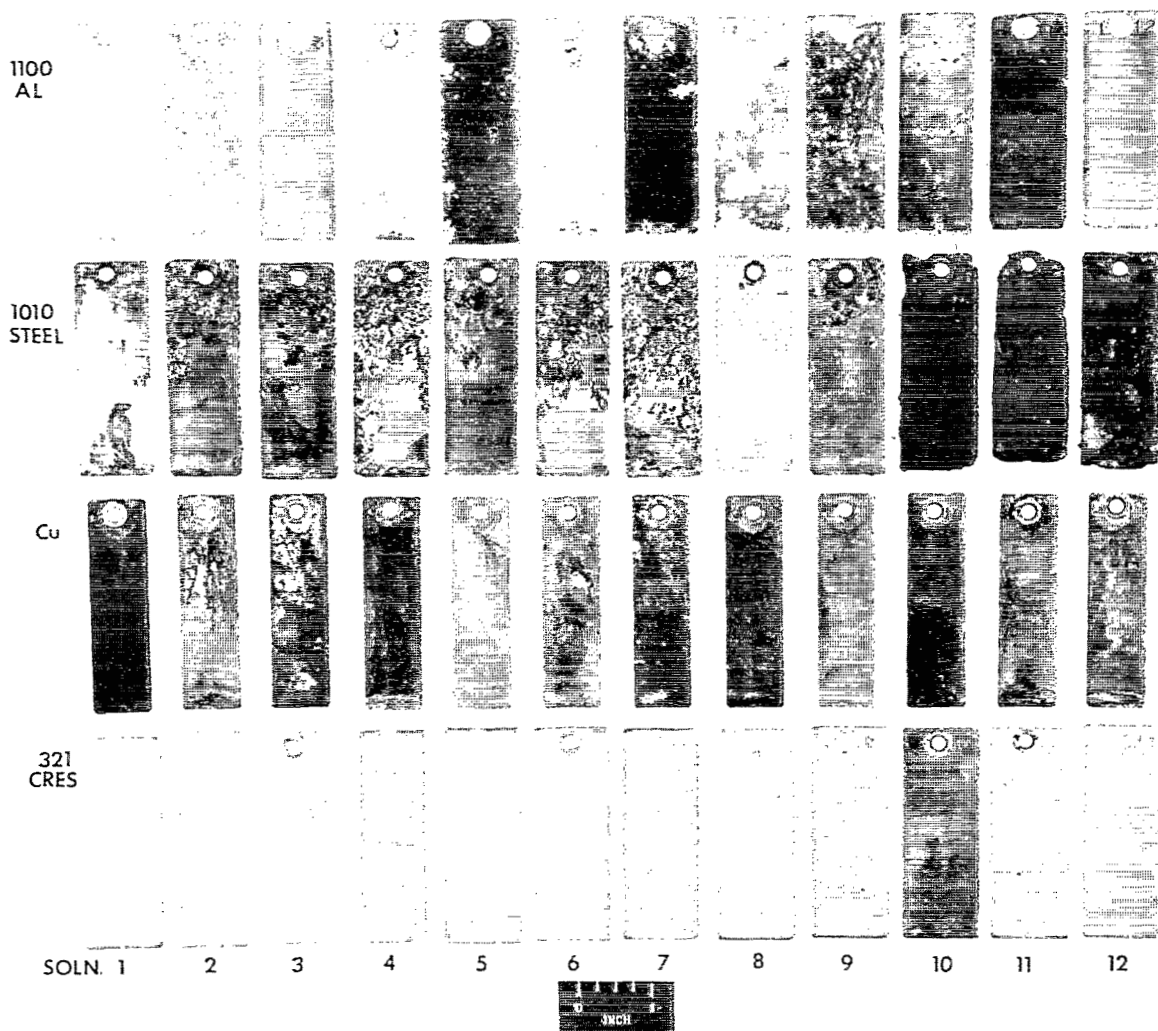


Figure 2. Appearance of elevated temperature test specimens.

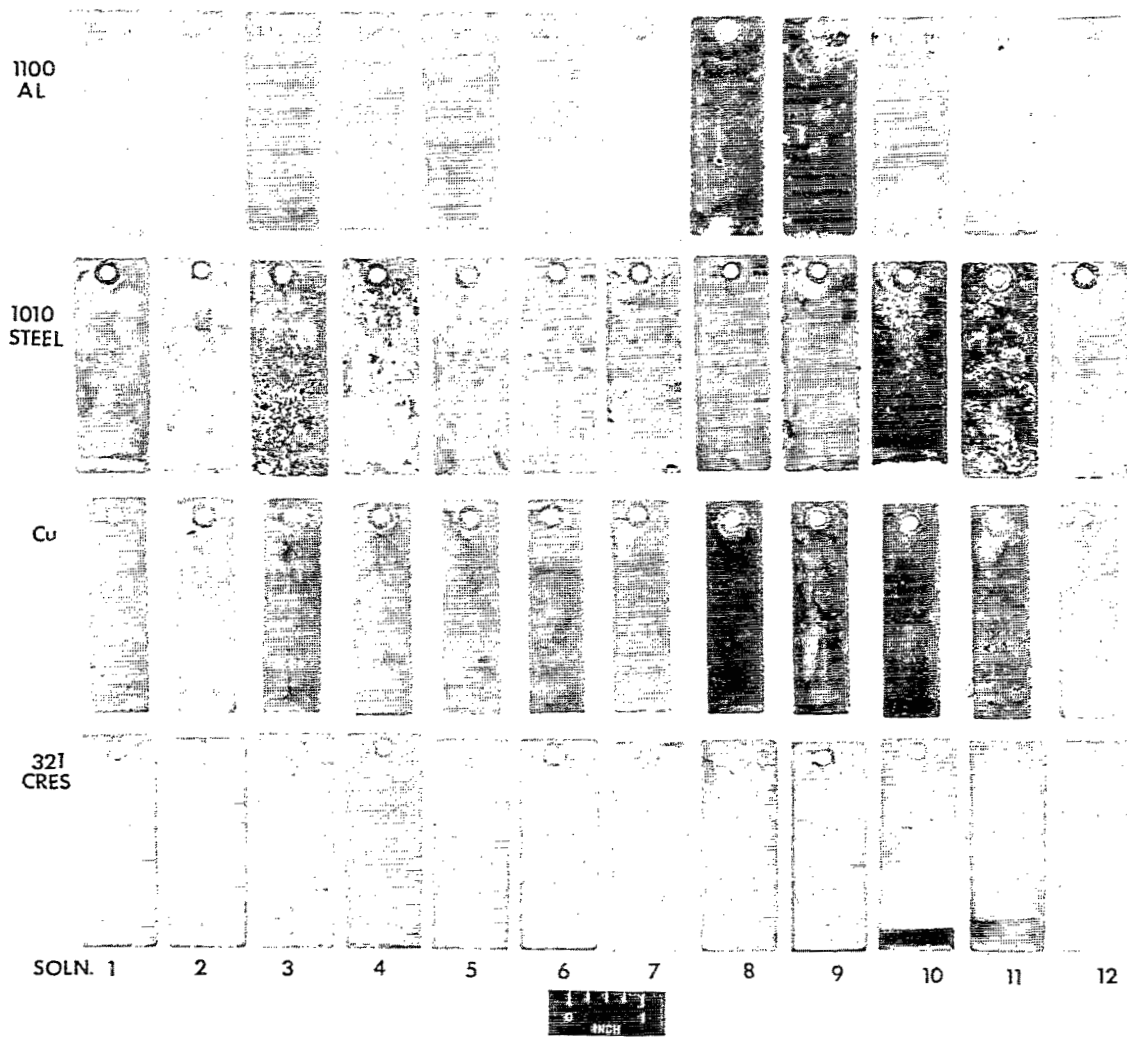


Figure 3. Appearance of room temperature test specimens.

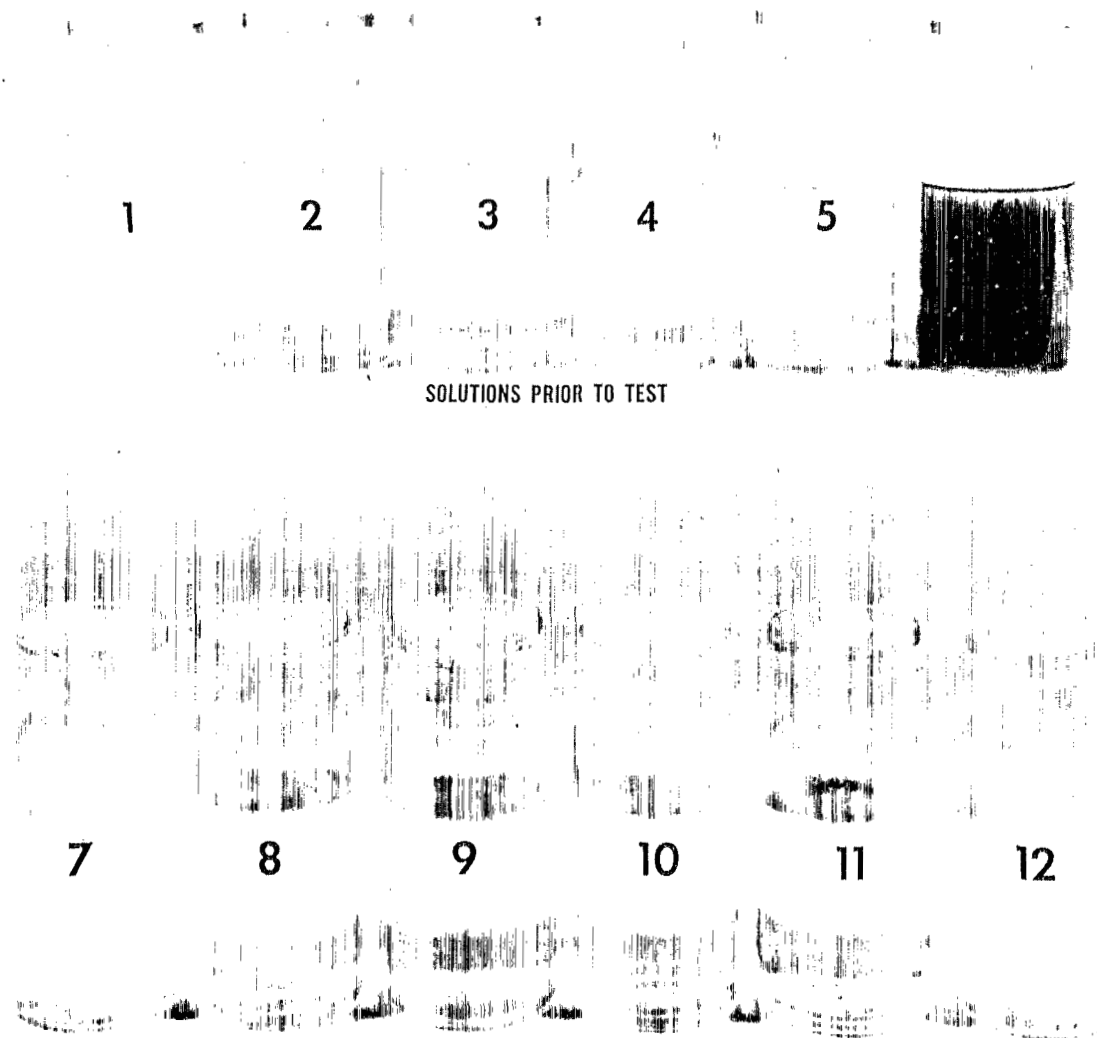


Figure 4. Freshly prepared test solutions.

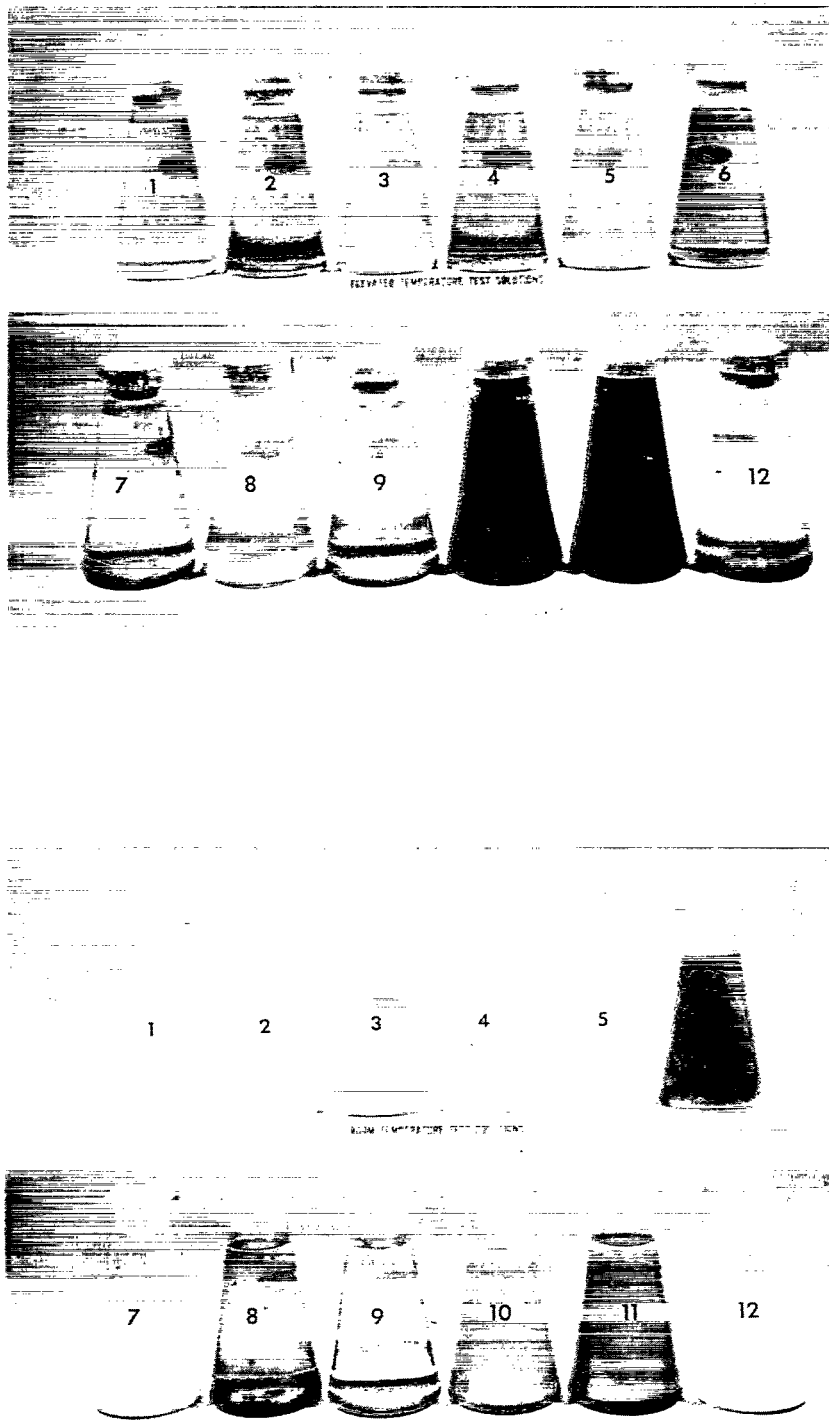


Figure 5. Test solutions after exposure.

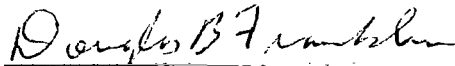
APPROVAL

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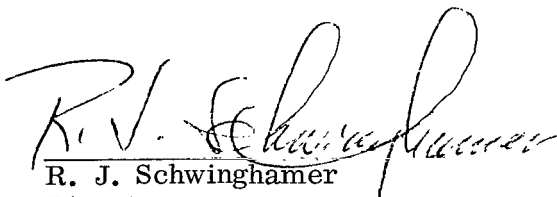
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